

Liquid Phase Hydrogenation of Benzene to Cyclohexene on Ruthenium Catalysts

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LIQUID PHASE HYDROGENATION OF BENZENE TO
CYCLOHEXENE ON RUTHENIUM CATALYSTS

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LIQUID PASTE REFORMATION OF LEMNINE IV.
CYCLOHEXANOL AND SUBSTITUTED ANALOGUES

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LIQUID PHASE
HYDROGENATION OF BENZENE TO CYCLOHEXENE
ON RUTHENIUM CATALYSTS

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Abstract The formation of cyclohexene in the hydrogenation of benzene on ruthenium catalysts have been studied. The influence of various reaction factors, e.g. hydrogen pressure, alkali concentration, amount of catalyst and temperature was investigated. Poisoning of the catalyst by FeSO_4, FeCl_3 and TiCl_3 resulted in much higher selectivities for cyclohexene than when non-poisoned catalysts were used. The hydrogenations were performed in an alkaline aqueous phase and the importance of water was shown. The catalyst and its precursor were studied by physical and chemical methods including N_2 adsorption, TEM, SEM, X-ray diffraction, sedimentation analysis, optical microscopy and ESCA. The non-poisoned reduced catalyst was shown to consist of metallic ruthenium. The iron poisoned reduced ruthenium catalyst consists of an Fe-Ru alloy covered by or embedded in iron hydrous oxides. The increased selectivity for the formation of cyclohexene on iron poisoned catalysts is explained as effects of low hydrogen coverage, decreased chemisorption of benzene and increased effectiveness factors. The titanium poisoned catalyst consists of metallic Ru and mixed ruthenium-titanium hydrous oxides. The rate of hydrogenation is correlated to the amount of metallic Ru in the catalyst.			
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LIQUID PHASE HYDROGENATION OF BENZENE TO CYCLOHEXENE
ON RUTHENIUM CATALYSTS

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The thesis consists of a summary and the following papers,
referred to in the text by their Roman numerals:

- I. Hydrogenation of Benzene to Cyclohexene on a Ruthenium Catalyst: Influence of Some Reaction Parameters.
C.U. Ingemar Odenbrand and Sten T. Lundin, J. Chem. Tech. Biotechnol. 1980,30,677.
- II. Hydrogenation of Benzene to Cyclohexene on an Unsupported Ruthenium Catalyst: Effects of Poisons.
C.U. Ingemar Odenbrand and Sten T. Lundin, J. Chem. Tech. Biotechnol. 1981,31,660.
- III. Hydrogenation of Benzene to Cyclohexene on a Ruthenium Catalyst: Physical and Chemical Characterisation of the Catalyst and its Precursor.
C.U. Ingemar Odenbrand and S. Lars T. Andersson, J. Chem. Tech. Biotechnol. 1982,32, In press.
- IV. Hydrogenation of Benzene to Cyclohexene on an Unsupported Ruthenium Catalyst: Physical and Chemical Characterisation of Iron Poisoned Catalysts in Relation to their Catalytic Performance.
C.U. Ingemar Odenbrand and S. Lars T. Andersson.

- V. Hydrogenation of Benzene to Cyclohexene on an Unsupported Ruthenium Catalyst: An ESCA Study of Titanium Poisoned Catalysts.

C.U. Ingemar Odenbrand and S. Lars T. Andersson.

Papers IV and V are submitted for publication.

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INTRODUCTION

The background for the work presented in this thesis is the potential use of cyclohexene as starting material for industrially important synthetic routes. The high reactivity of the double bond makes cyclohexene useful as an alkylating agent. It can also be used for the production of adipic acid used in the large scale fabrication of nylons. Another interesting application is in the production of maleic acid where increased yields are observed when the starting material cyclohexane is substituted by cyclohexene.

Existing production routes for cyclohexene use quite expensive raw materials such as cyclohexanol and chlorcyclohexane. If cyclohexene could be produced directly from benzene raw material costs would be cut by a large margin. These are some of the reasons for starting this projekt, a selective hydrogenation of benzene to cyclohexene, which is in line with other selective hydrogenations studied in our department.

Cyclohexene was detected among the products in the hydrogenation of benzene as early as in 1957¹. Nickel, in the form of a film, was used as a catalyst and the reaction was performed at low pressures and low temperatures (318 K). The amount of cyclohexene formed was minor but the selectivity was as high as 19%.

Hydrogenations in the liquid phase on a ruthenium black catalyst at 298 K yielded 0.18% cyclohexene². Addition of 5-50% of an aliphatic alcohol to the liquid benzene caused the yield to increase to 2.2%. This process, with a reaction temperature of 288 - 333 K, was claimed in a patent³.

In previous experiments with a Raney-W2 catalyst it was possible to increase the yield of cyclohexene to 0.5%⁴. The hydrogenations were performed in a stirred autoclave of stainless steel at a hydrogen pressure of 0.5 mPa and at a temperature of 454 K. The yield of cyclohexene was also shown to increase with temperature.

The promising results⁵, with yields up to 32%, indicated the use of ruthenium as a suitable catalyst and also to a more polar solvent for the hydrogenation. Later hydrogenation results obtained in an aqueous slurry with a poisoned ruthenium catalyst^{6,7} showed yield of cyclohexene of 20% at 454 K and a total pressure of 6.9 MPa. These interesting results prompted this detailed study of the selective hydrogenation of benzene to cyclohexene on ruthenium catalysts.

EXPERIMENTAL PROCEDURES

Hydrogenation apparatus and procedure

The hydrogenation of benzene was performed in a 1-dm³ Parr pressure reaction apparatus (series 4500). The reaction vessel was made of AISI-316-T stainless steel and equipped with an internal cooling coil. The temperature was measured with thermocouples inserted in a thermowell and regulated by an automatic temperature controller. The pressure was measured with manometers and a transducer. The stirring of the reaction solution performed by two 5.8 cm wide 45° pitched blade turbines with six blades on each turbine was at a rate controlled by an electric adjustable speed motor. The gases were supplied from cylinders at constant pressure and introduced to the base of the reactor. The entrance tube also served as a sampling tube for the liquid samples.

After introducing the catalyst, suspended in the aqueous phase, and benzene, the protecting gas (nitrogen or argon) was removed by evacuation to a pressure of 16 kPa. The temperature was then increased to the desired level. The reaction time was measured from the moment when hydrogen gas was introduced into the reactor. Liquid samples were withdrawn, and analysed as described below, at different intervals during the hydrogenation experiment

Catalyst preparation

The catalyst precursor was made by precipitation, at the desired pH and temperature, of an aqueous solution of ruthenium (III) chloride and various additives (mainly iron salts) at the addition of sodiumhydroxide. The precursor was then reduced in situ at the desired pressure and temperature during the first moments of the hydrogenation experiment. Details on the catalyst preparation technique are given in papers I-V.

Product analysis

The samples taken from the reactor were separated into three phases. From the upper, organic, liquid phase, samples were taken with a syringe and analyzed on a gas chromatograph (PYE series 104, model 54) equipped with a FID detector. The column (4.5 m long, 3 mm o.d.) was packed with 10% polyethylene glycol phenyl ether supported on 80 - 100 mesh Chromosorb P. The temperature in the column was 353 K and in the detector 423 K. Nitrogen was used as the carrier gas. The only products observed were cyclohexene and cyclohexane.

Corrosion measurements

In the early experiments corrosion products from stainless steel in the reactor walls was detected on the catalyst after use. To avoid this unwanted poisoning the inner parts of the reactor was covered with Teflon. In this context the rate of corrosion was measured by atomic absorption spectroscopy at various temperatures and pH:s.

Characterization of catalysts

The catalyst and its precursor were studied by various physical and chemical methods. The adsorption of N_2 at 77 K was used to measure the total surface area (S_{BET}) and also to study the pore system. Pore-size distributions were determined on a number of catalysts. The porosity of the catalyst was calculated from the total pore volume, measured on a Perkin-Elmer Shell model 212 D Sorptometer, and the density of the solid.

Some catalysts were also studied by adsorption of hydrogen, one of the reactants used in the hydrogenations.

Diffusion processes can severely limit the rate of reaction and, more important, they can decrease the yield of cyclohexene, which forms as an intermediate in the hydrogenation of benzene to cyclohexane. The pore diffusion resistance is largely dependent on the macroscopic particle size of the catalyst. The particle diameter was measured by sedimentation techniques, and by microscopy using a scanning electron microscope, JEOL JSM-U3, and a stereo visible light microscope. The chemical composition of the catalyst was determined by XRD and ESCA. The X-ray diffraction studies were performed on a Philips PW 1310 powder diffractometer with a PW 1050 wide-angle goniometer. These studies produced results both on the crystalline chemical compounds present in the catalyst and also on the crystallite size. The ESCA measurements were performed on an AEI ES 200B electron spectrometer equipped with an Al-anode (1486.6 eV). Quantitative ESCA analysis was performed using peak areas measured with a planimeter. Some spectra were digitized and smoothed on a Textronix 4051 with a 4662 interactive digital plotter. Peak areas were then evaluated by a numeric method.

REACTIONS, REACTION CONDITIONS AND EVALUATION OF DATA

In a standard hydrogenation 100 cm³ benzene (1.123 mol) is reacted with hydrogen at a constant pressure of 3.4 MPa. The catalyst, typically 0.11 g Ru metal, is suspended in 400 cm³ of an alkaline aqueous phase. The stirring rate was 1200 rev. min⁻¹ in most cases.

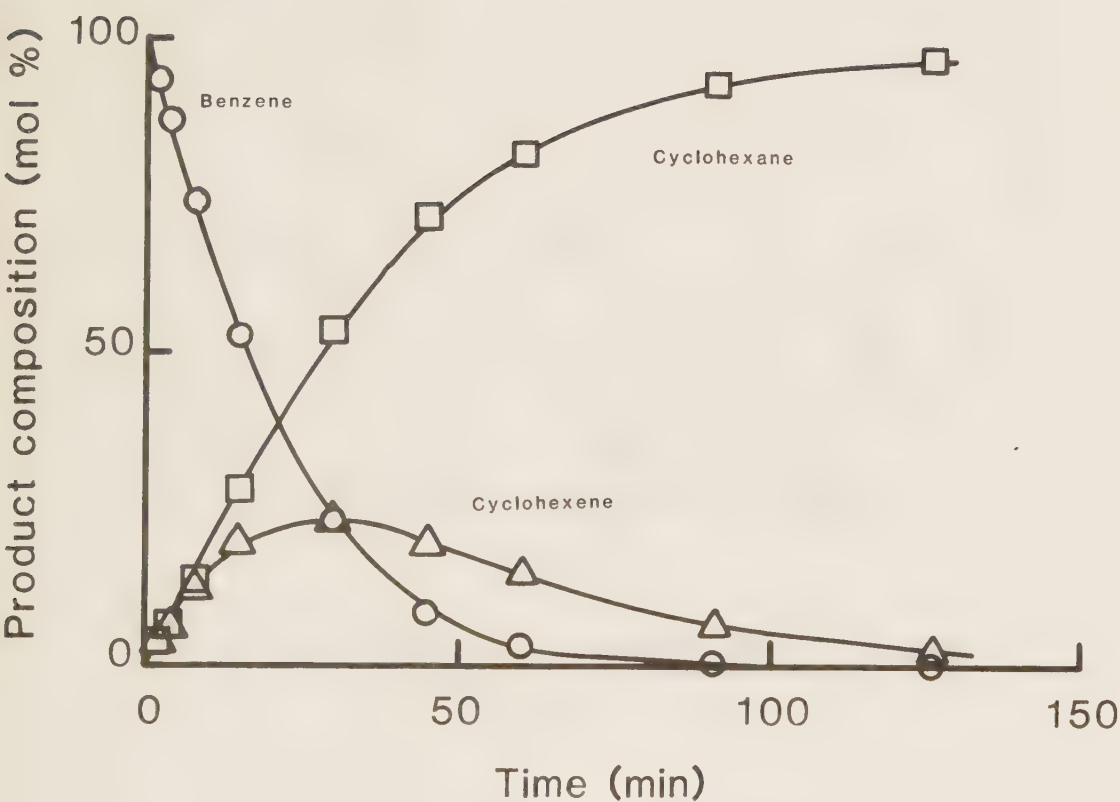


Figure 1 Product composition as a function of reaction time

Figure 1 shows the product composition as a function of the reaction time for a typical hydrogenation. The example shown in the figure was performed with a catalyst poisoned with 20 atom % Fe at 431 K in 1.19 M NaOH. The rate of reaction of all components is evaluated as the slopes of the concentration versus time curves. The rates are essentially first order in

the concentration of benzene and cyclohexene. As the figure shows cyclohexene is an intermediate in the hydrogenation of benzene to cyclohexane. Therefore, as the conversion of benzene increases the concentration of cyclohexene increases, reaches a maximum and decreases at higher conversions. This maximum defines the maximum yield discussed in this thesis and it is obtained at different conversions depending on the reaction condition used.

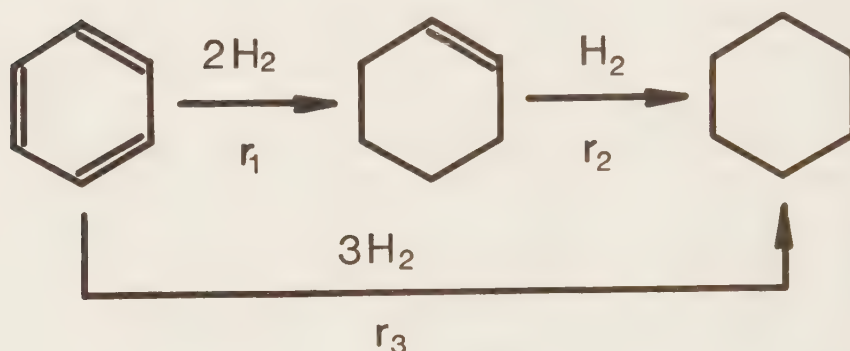


Figure 2 Reaction scheme for the hydrogenation of benzene to cyclohexene and cyclohexane

The rate of formation of the endproduct, cyclohexane, is not zero at zero conversion. This indicates that there might exist two hydrogenation routes as illustrated in Figure 2. The apparent direct route can be explained as a pore diffusion or an adsorption-desorption disguise of the true reaction sequence⁸. Experiments performed under conditions where the pore diffusion is insignificant show that there is still a direct route. However, the adsorption-desorption effect still remains as a plausible explanation.

MASS TRANSFER

The reaction system is rather complex and the reaction itself is conducted in a slurry reactor where many different mass transfer steps could be involved. There are four phases present. The solid phase is the catalyst with particles in the range 1 - 50 μm . There are two liquid phases present, one, the continuous phase, the aqueous phase, and one organic phase. The organic phase, a mixture of benzene, cyclohexene and cyclohexane, is dispersed as small drops with a diameter of 0.05 to 0.14 mm. The hydrogen gas is also present in a separate phase both as bubbles with diameters from 0.1 to 0.9 mm and as a headspace above the liquid phase.

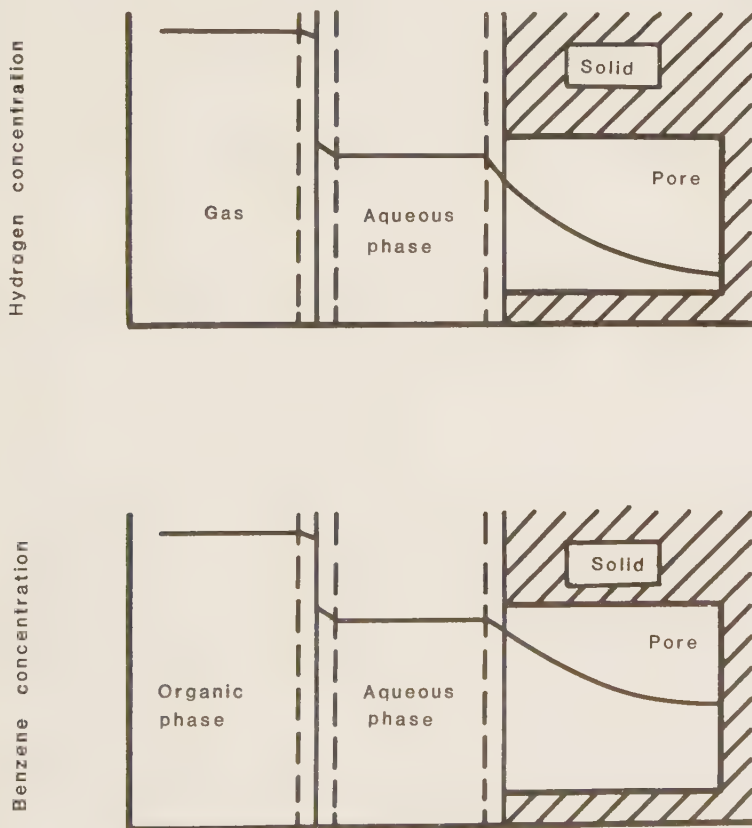


Figure 3 Concentration profiles for hydrogen (top) and benzene (bottom) in a four phase system

Figure 3 illustrates the mass transfer resistances for benzene and hydrogen.

The mass transport steps for hydrogen are: (i) diffusion within the gas bubble: (ii) gas-liquid film diffusion around the gas bubble: (iii) liquid-catalyst film diffusion around the catalyst particle: and (iv) pore diffusion within the catalyst particle.

The mass transport steps for benzene are: (i) diffusion within the drop: (ii) liquid-liquid diffusion through the film around the drop: (iii) see above: (iv) see above.

The effects of mass transfer can be dealt with in two ways: experimental determination of mass transfer rates and calculative approaches. Both methods have been used in this thesis. Details are given in papers I, II and IV.

SUMMARY OF PAPERS

Paper I: Hydrogenation of Benzene to Cyclohexene on a Ruthenium Catalyst: Influence of Some Reaction Parameters.

The hydrogenations were performed in an alkaline aqueous phase in a stirred autoclave of stainless steel. The purpose of the studies was to scan reaction factors in order to establish optimal conditions for the production of cyclohexene. A measured quantity of a stock solution of ruthenium(III) chloride in water was introduced into the reaction vessel at room temperature (293 K). The reaction bomb was assembled and then flushed with nitrogen gas with stirring. Then 100 cm³ of benzene was introduced into the reactor and after 10 min of stirring ruthenium hydroxide precipitated at the addition of sodium hydroxide solution. The catalyst was reduced in situ at the desired pressure and temperature. The volume of the aqueous phase at the start of the experiment was 400 cm³.

The reaction was approximately first order in the concentration of benzene as shown in Figure 2. Two linear parts are achieved when the logarithm of the molar fraction of benzene in the organic phase is plotted against time. This behaviour can be explained by inhibition of the reaction by adsorbed hydrocarbons, benzene and cyclohexene, on the catalyst according to a Langmuir-Hinshelwood rate expression. At higher temperatures especially above 440 K the poisoning of the catalyst by corrosion products causes a considerable drop in activity as the reaction proceeds. Therefore initial rate data were used as a measure of the catalyst's activity.

The influence of the stirring rate on the overall rate of hydrogenation of benzene was studied at 387 K, 3.4 MPa H₂ at a catalyst loading of 0.426 g Ru metal in 3.6 NaOH. The initial rate of reaction was shown to be independent on the stirring rate above around 600 rev. min⁻¹. All the following experiments were performed at a stirring rate exceeding 720 rev. min⁻¹.

The influence of the resistance to gas-liquid mass transfer is thus insignificant compared to other resistances at this temperature.

The influence of the hydrogen pressure was studied at 447 K between 0.9 and 3.5 MPa. Figure 4 illustrates a first order dependence of the initial rate on the hydrogen pressure. The maximum yield of cyclohexene was also increasing from 6 to 19% with a tendency to level off at higher pressures.

The influence of the concentration of NaOH was studied at 448 K between 0.1 and 7 M. The rate dropped sharply when the concentration was increased from 0.1 to 1.2 M NaOH. At higher concentrations the drop in rate was still considerable and could be correlated to the solubilities of hydrogen and benzene in the aqueous phase. There is an optimal NaOH concentration for maximum yield of cyclohexene and this is 3.6 M at 448 K.

Mass transfer calculations showed that the external gradient for hydrogen increases rapidly with decreasing NaOH concentration. At NaOH concentrations above 1 M the gradient for benzene is less than 10% and increases to 40% in 0.1 M-NaOH. This results in very marked decrease in the maximum yield of cyclohexene.

The temperature is the factor which influences the yield to the greatest extent. In 3.6 M NaOH, with a catalyst loading of 0.426 g Ru metal and at a stirring rate of 715 rev. min⁻¹, the yield increased with the temperature from 3% at 390 K to 16% at 480 K. The Arrhenius plot of the rate of hydrogenation between 360 and 460 K yields an apparent activation energy for the overall process of 22 kJ mol⁻¹. This low value indicates some influence from diffusion processes. A rate maximum was observed at 460 K in accordance with results in literature.

The influence of the amount of catalyst was studied at 448 K, 3.5 MPa H₂ in 3.6 M NaOH and at a stirring rate of 1125 rev. min⁻¹. The yield of cyclohexene increases with the amount of catalyst from 7 to 19% as the loading is increased from 0.042

to 0.425 g Ru metal. The rate increases first in a linear manner with increasing load but at higher loads the rate increase is lower. This is also an indication of the fact that the overall process is chemically controlled at low loadings but diffusion controlled at higher loadings.

An evaluation of the gas-liquid mass transfer resistance was performed and $k_L a$ was found to be 0.64 s^{-1} under these reaction conditions. Table 2 illustrates the effects of the gas-liquid resistance at various loadings. At high loadings this resistance is very large leading to a concentration drop of 56% of the solubility of hydrogen in the gas-liquid film. Even at the lowest catalyst amount the mass transfer resistance is considerable (14%). At 448 K the rate is thus shown to be greatly influenced by diffusion of hydrogen. The internal gradient for benzene, calculated for a particle size of $13.3 \mu\text{m}$, is only 9% at the lowest loading and only 5% at the highest. These small internal gradients in combination with a low hydrogen concentration on the catalyst surface favours the formation of cyclohexene.

Ruthenium catalyst are poisoned by small amounts of less active metals like Ni, Co and Fe. The rate of corrosion of the reactor walls was measured at 446 K and was found to be considerable ($19 \text{ mg metal dissolved h}^{-1}$). At 387 K the scatter in the yield of cyclohexene was quite large (1.1 - 3.5%). Recalculation of the rate of corrosion led to the correlations shown in Figures 13 and 14. There were excellent linear correlations between both the yield of cyclohexene and the rate of hydrogenation and the amount of metal. The poisoning of the ruthenium catalyst by < 1% of less active metals such as Fe, Cr and Ni was thus shown to cause a great scatter in both the yield of cyclohexene and the rate of hydrogenation. And more important, it was shown that an increased amount of poisoning of the catalyst led to an increased yield of cyclohexene.

Paper II. Hydrogenation of Benzene to Cyclohexene on an
Unsupported Ruthenium Catalyst: Effects of Poisons.

Earlier investigations showed that iron and other metals accidentally corroded from the stainless steel in the reactor increased the yield of cyclohexene substantially. Therefore a study of the effect of iron on the catalyst performance was undertaken. The effect of addition of TiCl_3 was also studied since this compound was found by others to increase the yield of cyclohexene.

In the poisoning experiments, FeSO_4 or TiCl_3 was added to an aqueous solution of RuCl_3 in the reactor at room temperature (293 K). In Series A a stock solution of FeSO_4 was used and in Series B FeSO_4 was added as a freshly prepared solution. The precipitation of the catalyst precursor was performed under N_2 and occurred inside the reactor at the addition of 9.6 M NaOH to a final concentration of 1.19 M. This concentration was used throughout this paper. The walls of the reactor were covered with Teflon to minimize the rate of corrosion. This procedure was used for the catalysts discussed in part 3.1 to 3.5 of paper II. The other catalysts were precipitated in a glass vessel at 293 or 353 K.

Mass transport limitations were estimated by the size of the apparent activation energy which was increased from 22 to 31 kJ mol^{-1} when the hydrogenations were performed with a smaller amount of catalyst and a higher rate of stirring at temperatures between 315 and 390 K. Since mass transfer effects were still considered to be important experimental determination of $k_L a$ was performed at 391 K. The influence of the gas-liquid hydrogen mass transfer was then less than in Paper I and the concentration drop was 5 - 18% of the solubility of hydrogen. The value of $k_L a$ was increased greatly to 7.8 s^{-1} .

Figures 1 and 2 show that the effect of iron was different in Series A and B. An optimal poisoning degree was obtained in both cases with a small difference in the maximum yield but

with a greater difference in the poisoning level needed for this maximum. The rate dependence was also different and the addition of a stock solution of FeSO_4 resulted in a much stronger poisoning effect than when FeSO_4 was introduced as a fresh solution. If the maximum yield of cyclohexene is plotted against the rate of hydrogenation as in Figure 3 an interesting result appears. The yield is decreasing with increasing rate and the different preparations fall on the same curve. This means that when the rate is decreased to the same extent on two different catalysts the same yields of cyclohexene are obtained. This effect is discussed further in Paper IV.

The effect of poisoning on the yield of cyclohexene is discussed and explained as a geometric effect. The dilution effect of iron in the ruthenium matrix will be discussed further in Paper IV. The effect of corrosion products was shown to be negligible at the conditions used. ESCA measurements of the rate of corrosion was in excellent agreement with atomic absorption measurements.

When TiCl_3 is used as a poison there is also an optimal degree of poisoning (Figure 4). A higher amount of cyclohexene is obtained on an unpoisoned catalyst in this series. This can be explained by corrosion products their effect being larger on the smaller amounts of catalyst used. The rate of hydrogenation decreases continuously with an increasing titanium content. The activity levelled off at high titanium contents still with some activity left in contrast to what was observed for the iron poisoned catalysts. The poisoning mechanism could be similar to the mechanism described for the iron poisoning, but ESCA revealed that an increased amount of oxidized ruthenium was present on catalysts with high titanium contents. This effect is discussed further in Paper V.

The effect of oxygen on the rate of hydrogenation is large as shown in Figure 6. The use of protecting gases and evacuation of the reactor are thus very important to achieve high activities.

Of an utmost importance for the production of cyclohexene is the presence of an aqueous phase. When the reaction was carried out in pure benzene no cyclohexene was detected. The catalyst used was earlier used in an aqueous phase and gave normal yields of cyclohexene. The effect of water can be explained on kinetic grounds considering the fact that the solubility of cyclohexene is only 12% of the solubility of benzene in water. This obviously leads to a decreased rate of hydrogenation of cyclohexene normally considered to be much higher than the rate of hydrogenation of benzene. It could also be explained as an effect of water molecules repelling the cyclohexene molecules from the catalyst surface thereby decreasing the strength of adsorption of cyclohexene and as a consequence increasing the rate of its desorption from the active sites.

When the hydrogenations were performed at 316 K the catalyst precursor was not reduced immediately at the addition of the hydrogen gas. The induction period observed also resulted in a decreased yield of cyclohexene (Figure 7). If the catalyst was prereduced with hydrogen at atmospheric pressure in the aqueous phase for 1 hour at 293 K an increased yield of cyclohexene was obtained.

Each hydrogenation experiment was performed with a new batch of freshly prepared catalyst. A standard catalyst preparation procedure was developed in which the precursor was precipitated at 353 K in a glass vessel using N_2 or Ar as protecting gases. The reproducibility of the performance of these catalysts was very good (yield $6.2 \pm 0.3\%$ at 318 K, 3.65 MPa H_2 , 0.11 g Ru metal).

When the catalyst is poisoned with $FeCl_3$ and the hydrogenation is performed at 318 K, 3.75 MPa H_2 both the yield of cyclohexene and the rate of hydrogenation of benzene decrease with increasing iron content. This result is in contrast to results obtained at 388 K where both $FeSO_4$ and $FeCl_3$ additions increased the yield of cyclohexene to about the same extent. The reasons for the discrepancy is obscure and cannot be explained as a mass transfer effect. Measurements of the iron content in the cata-

lyst in this series revealed that some of the iron present in the catalyst is not removed by dissolution by hydrochloric acid (pH 1) for one week at 293 K. This amount is supposed to be alloyed to ruthenium.

There is an optimal pressure (around 4 - 5 MPa) both for the rate of hydrogenation and for the yield of cyclohexene (Figure 10). The initial rate of hydrogenation of benzene can be correlated to a Langmuir-Hinshelwood expression shown below.

$$r_A^0 = \frac{k b_A C_{Ao} (b_{H_2} p_{H_2})^3}{(1 + b_A C_{Ao} + (b_{H_2} p_{H_2})^{1/2})^7}$$

The rate data correlate excellently to the expression given but no mechanistic conclusions can be drawn from this formula since mass transport effects are suspected to be considerable. Nothing is known about the particle size of the catalyst in this system but calculations performed for catalysts with a diameter of 14 μm show that the external gradients of both hydrogen and benzene are very large. In fact the concentration on the surface approaches zero at low pressures. The changing reaction order for benzene might be explained as a mass transfer effect with transport of hydrogen being the limiting step at pressures below 3 MPa H_2 . The dependence of the yield of cyclohexene on the hydrogen pressure can be explained if the rates in the different routes in Figure 12 are different functions of the hydrogen pressure.

Paper III. Hydrogenation of Benzene to Cyclohexene on a Ruthenium Catalyst: Physical and Chemical Characterization of the Catalyst and its precursor.

Earlier papers have indicated influence of mass transport on the yield of cyclohexene. However, indices, e.g. porosity, particle diameter and pore-size distributions were needed for future mass transport calculations. Information on the chemical state of ruthenium in the catalyst is needed in order to achieve a better understanding of the chemistry of the hydrogenation of benzene to cyclohexene. Rates are normally expressed on a surface area basis so this property need to be determined too.

The catalyst precursors were precipitated in a double-walled glass vessel at 353 K by instantaneously adding 9.6 M-NaOH to an aqueous solution of RuCl_3 ($5 \text{ g dm}_{\text{aq}}^{-3}$). The final concentration of NaOH was 1.19 M. The precipitate was then aged for one hour under an argon stream. Reduction of the precursors to active catalysts was performed in a stainless steel reactor with Teflon-covered walls at 318 K and 3.6 MPa H_2 while stirring (20 rev.s^{-1}) for one hour. Both materials were washed and dried by evacuation at 293 K before examination. Adsorption isotherms measured on the reduced catalyst and its precursor indicate a great difference in pore sizes. The pore-size distribution (Figure 2) shows a close resemblance in the pore structure for the catalyst and its precursor. The distributions are wide with several maxima. The precursor has most of its pore volume in pores with a diameter $> 8 \text{ nm}$. The surface area is greatly increased from 27 to $112 \text{ m}^2 \text{g}^{-1}$ during the reduction. Evaluation of the surface area by the t-method reveals that both the precursor and the catalyst are compounds without microporosity. The surface area contained in pores with a diameter $< 8 \text{ nm}$ is 17% for the precursor and 47% for the reduced catalyst. The reduction thus creates a large amount of small pores, thereby increasing the total surface area considerably. The total pore volume is increased to twice its original value during the reduction and the amount of pore volume in the pores with diameters $> 40 \text{ nm}$ is around 30%. The catalyst produced by reducing

the hydroxide in an alkaline aqueous phase at 318 K has good characteristics: a high surface area ($110 \text{ m}^2 \text{ g}^{-1}$) and a wide distribution of pores to accomplish an easy transport of reactants and products to and from the active sites on the catalyst surface.

The main factor, influencing the pore diffusion is the catalyst particle size. The reduced catalyst consists of a distribution of spherical particles with diameters in the range 2 to 70 μm . The surface average diameter, calculated from the distributions shown in Figure 6 increases from 25 to 40 μm as the initial concentration in the precipitation solution is increased from 0.75 to 5.00 $\text{g RuCl}_3 \text{ dm}_{\text{aq}}^{-3}$.

The SEM measurements included X-ray energy dispersive analysis. No corrosion products such as Fe, Ni or Cr could be detected which implies that the rate of corrosion is quite low at 318 K. Both the reduced catalyst and its precursor consisted of Ru with small amounts of Si and Ca evenly distributed over the catalyst. Si and Ca are dissolved from the glass vessel during the preparation procedure.

The X-ray diffraction pattern is shown in Figure 7. Both the catalyst and its precursor exhibit broad and weak diffraction lines caused by small particle sizes. The precursor consists of a hydrous oxide of ruthenium. The reduced catalyst shows peaks characteristic for metallic Ru. The X-ray diffraction analysis thus shows that the reduced catalyst consists of metallic Ru with minor amounts of hydrous oxide remaining from the precursor.

The crystallite size obtained by X-ray line broadening is 1.9 nm for the precursor and 3.4 nm for the reduced catalyst. TEM yielded values of 2.0 and 3.0 nm respectively. Calculation of the size from S_{BET} , with the assumption of free spherical particles, yields a value of 4.4 nm which is in fair agreement with the X-ray and TEM values.

ESCA measurements on the precursor yielded a binding energy for

Ru $3d_{5/2}$ of 281.5 eV which lies between 281.6 for $RuCl_3 \cdot 3H_2O$ and 281.4 for $RuO_2 \cdot xH_2O$. This indicates the presence of Ru in an oxidized state. The broad peaks obtained reflect the presence of both Ru (III) and Ru (IV) in the precursor. When the used catalyst was investigated problems arose caused by the possibility of oxidation of the catalyst when it was inserted into the spectrometer. If the catalyst suspension was placed in the spectrometer and dried by evacuation Spectrum 8 C was obtained. The pattern looks like the pattern obtained from a highly charged ruthenium species but can be explained as C 1s peaks from pump oil contamination (285.0 eV) and CO_3^{2-} (290.0 eV). If the sample is scratched the appearance of a Ru $3d_{5/2}$ peak at 279.9 eV is noticed (Figure 8 D). Clean spectra were obtained by washing the catalyst by NaOH solutions of pH < 11. During the initial part of the hydrogenation the precursor hydroxide is reduced and metallic ruthenium is formed. When the catalyst is washed with HCl the Ru $3d_{5/2}$ BE decreased to 279.8 eV and the FWHM from 1.9 to 1.7 eV. This indicates the presence of a small amount of ruthenium hydrous oxides in the original catalyst.

The O 1s spectra of the precursor are broad and can be assigned to OH^- (531.1 eV) and O^{2-} (529.4 eV) which corresponds well to a hydrous oxide. The reduced catalyst (pH 7) shows a similar structure which indicates the presence of a small amount of hydrous oxide. Washing at pH > 7 increased the OH^- component as a result of the NaOH left on the catalyst on evaporation. Washing with HCl removed the peak at 529.3 eV in correspondence to a dissolution of hydrous ruthenium oxides.

Corrosion products are known to poison the catalyst. The amounts of Fe and Cr on the catalyst have been measured by ESCA. Ni have not been measured because of the low intensity of the Ni $2p_{3/2}$ peak. Both Cr and Fe occurs as hydrous oxides similar to those in the protective layer on the stainless steel surface. The Fe/Ru ratio by ESCA is approximately the same as the AAS value. The corrosion products are thus shown to be present as separate phases poisoning the catalyst by surface or pore blocking.

Paper IV. Hydrogenation of Benzene to Cyclohexene on an Unsupported Ruthenium Catalyst: Physical and Chemical Characterization of Iron Poisoned Catalysts in Relation to their Catalytic Performance.

Iron has a pronounced positive effect on the yield of cyclohexene. The yield is expected to be influenced by poisoning of the catalyst surface but also by the pore diffusion. Therefore it is of interest to try to correlate changes in physical and chemical characteristics of the catalyst to its catalytic performance in the hydrogenation of benzene to cyclohexene.

The catalyst precursors were precipitated in a glass vessel at 353 K by instantaneous addition of 9.6 M-NaOH to an aqueous solution of RuCl_3 and FeSO_4 or FeCl_3 . The final concentration of NaOH was 1.19 M and the precipitation was performed under an argon atmosphere. The precursors were reduced at 3.5 MPa H_2 at 318 or 373 K.

The X-ray diffraction analysis was performed on washed and passivated catalysts with varying iron content. All catalysts, made by coprecipitation of RuCl_3 and FeSO_4 , with an iron content below 30% show a pattern characteristic of metallic ruthenium. When the iron content is increased peaks from Fe_3O_4 also appear in the spectra. Catalysts made from RuCl_3 and FeCl_3 consist of metallic Ru and $\alpha\text{-FeO(OH)}$.

Non-passivated catalysts sintered on immediate exposure to air. The sintering of the Ru crystallites was accompanied by the appearance of bulk RuO_2 . A slow admission of O_2 to a 10% Fe-Ru catalyst resulted in a sintering of the metallic Ru crystallites but no bulk oxide was formed. In an FeCl_3 preparation at iron contents above 40% the small Ru crystallites are not sintered while the $\alpha\text{-FeO(OH)}$ crystallites are. The samples investigated by X-ray diffraction were normally not used in hydrogenations. Analysis of 15% Fe-Ru used catalysts, prepared from FeSO_4 and FeCl_3 , gave the same result as the

unused ones. It was also shown that all catalysts made from RuCl_3 and FeSO_4 always contained Fe_3O_4 while those made from RuCl_3 and FeCl_3 or $\text{Fe}(\text{NO}_3)_3$ contained $\alpha\text{-FeO}(\text{OH})$.

The crystallite size for the metallic Ru decreased from 4.0 nm to 3.1 nm as the amount of iron increased to 60%. This effect is a result of an increased amount of strain and faulting caused by the iron inserted into the ruthenium matrix.

The interplanar spacing in the Ru matrix is altered when the iron content is increased. There is a linear decrease with the iron content up to 30%. The linear dependence indicates the formation of an alloy between Fe and Ru. The amount of iron which is alloyed to ruthenium is estimated as 34% and the rest is present as oxides only detected by XRD at iron contents above 30%.

ESCA investigations showed that in all catalysts the Ru was present in the metallic state. Used catalysts contained iron in both an oxidized and a metallic state (Figure 4 F). The O 1s spectra showed the presence of oxygen species with the same binding energies as those of Fe_3O_4 and $\alpha\text{-FeO}(\text{OH})$. An increase in the iron content is associated with an increase in the oxygen content on the surface and this oxygen is evidently due to the presence of iron hydrous oxides. In Paper II the iron containing catalysts were precipitated in two ways. In series A the catalyst was precipitated from RuCl_3 and a stock solution of FeSO_4 and in series B a fresh solution of FeSO_4 was used. The ESCA analysis showed that the amount of iron in the surface differed greatly between series A and B. In Figure 8 the values of Fe/Ru obtained by ESCA is used to correlate the catalytic performance. With increasing iron content the rate decreases and both series fall on the same line in contrast to what is observed when it is plotted against the nominal ratio (Paper II). The maximum yield of cyclohexene increases to a maximum around Fe/Ru 0.16 and both series fall on the same line in this case too. Thus there is no difference in the catalytic performance of catalysts in series A and B if they are compared at the same Fe/Ru ratio in the catalyst

surface. The differences are explained as an effect of different crystallite sizes in series A and B.

The maximum yield of cyclohexene is obtained at an Fe/Ru ratio of 0.16. That is every 6th Ru atom is blocked. Above this poisoning level the probability of forming ensembles of six Ru atoms needed for planar adsorption of benzene decreases rapidly. The decrease in selectivity above Fe/Ru 0.16 can be explained by a lower tendency for benzene to be hydrogenated compared to cyclohexene.

The HCl washed catalysts show a higher metallic Fe content and are stable towards oxidation. This leads to the conclusion that an Fe-Ru alloy is formed. These alloy particles are embedded in or covered by iron hydrous oxides. All reactants, benzene, cyclohexene and hydrogen, are known to be chemisorbed on non-poisoned Ru-surfaces. On an Fe-Ru alloy literature data show that the amount of hydrogen chemisorbed decreases drastically with increasing iron content. We have also noticed the same phenomenon. The iron oxides, α -FeO(OH) and Fe_3O_4 , do not chemisorb hydrogen according to our measurements. The amount of chemisorbed benzene is also lower on Fe than on noble metals. The decreased rate and the increased selectivity at low iron contents is caused by a decrease in active surface area due to blocking by iron oxide phases and due to a decreased hydrogen and possibly benzene coverage on Fe-Ru alloy.

The total surface area decreases from $108 \text{ m}^2 \text{ g}^{-1}$ to $56 \text{ m}^2 \text{ g}^{-1}$ when the iron content is increased to 40%. The surface area that adsorbs hydrogen dissociatively decreases from 108 to $39 \text{ m}^2 \text{ g}^{-1}$ when the iron content is increased to 40%.

The pore volume is dependent on at least two factors: A low RuCl_3 concentration gives a more porous catalyst and a high iron content gives a less porous catalyst. The pore-size distributions show that the structure of the non-poisoned catalyst is retained on poisoning with iron. Figure 13 illustrates the specific rate of hydrogenation of benzene ($\text{rate}/S_{\text{H}_2}$) as a

function of the iron content. The rate decreases more rapidly than S_{H_2} , especially above 20% Fe. This can be an effect of a decreased chemisorption of benzene caused by the inability to form large ensembles of Ru atoms when the iron content is high.

The macroscopic particle size, an important factor for mass transfer, is greatly influenced by iron addition. A non-poisoned catalyst consists of particles between 5 and 50 μm diameter. At 30% iron no particles larger than 25 μm were detected. Figure 15 shows the surface average diameter as a function of the iron content for $FeSO_4$ and $FeCl_3$ preparations. The particle size is constant up to 15-20% Fe and decreases drastically at higher additions. These measurements were performed on catalysts stored for 14 days, but measurements within 15 minutes after the samples were withdrawn from the reactor showed that the actual size is about half the ones shown in Figure 15.

Since cyclohexene is an intermediate in the hydrogenation of benzene to cyclohexane its yield is expected to depend strongly on pore diffusion effects. The overall effectiveness factors were therefor calculated, after assuring that isothermal conditions prevailed, with the assumption of the following rate expression:

$$r_A = \eta \cdot k \cdot w \cdot C_A \cdot C_H$$

Experimental rate and selectivity data were obtained at 390 K, 3.5 MPa H_2 , 0.11 g Ru, 1200 rev.min⁻¹ in 1.19 M-NaOH. The influence of the resistance in the gas-liquid film was determined experimentally and the other resistances were estimated by procedures given in literature. Figure 16 shows the overall effectiveness factor which remains constant at around 0.2 below 15% Fe, then drastically increases to values around 0.9 at 25% Fe. At 30% Fe the overall process is kinetically controlled. The yield of cyclohexene is correlated to the overall effectiveness factor in Figure 17. The yield is increasing from 5 to 10% at iron contents between 0 and 15%. This increase is an effect of poisoning only since the effectiveness factor is constant.

Between 15 and 25% Fe the yield increases further as a result of both an increased poisoning and an increased effectiveness factor. The yield decreases above 25% Fe because of a severe blocking of active sites resulting in a high rate of hydrogenation of cyclohexene compared to the rate of hydrogenation of benzene.

The effects of poisons can be explained if the hydrogenation of benzene is assumed to follow two different routes. The hydrogenation of benzene to cyclohexene requires four hydrogen atoms and the direct route to cyclohexane requires six hydrogen atoms. Since the hydrogen coverage on the catalyst decreases with an increasing Fe content the route to cyclohexene is favoured. This first effect is observed in the whole Fe content range studied. The second effect, decreasing the yield of cyclohexene at iron contents above the optimal one, is the decreasing chemisorption of benzene at high Fe contents. The large ensembles necessary for the planar adsorption of benzene are easily destroyed on poisoning. Hydrogenation of cyclohexene requires smaller ensembles not so easily poisoned. This obviously leads to a decreased yield of cyclohexene at high Fe contents.

Paper V. Hydrogenation of Benzene to Cyclohexene on an
Unsupported Ruthenium Catalyst: An ESCA Study
of Titanium Poisoned Catalysts.

It has been shown that poisoning of the Ru catalyst with various poisons, e.g. TiCl_3 , results in an increased yield of cyclohexene. The rate of hydrogenation of benzene decreases with an increased Ti content but levels off at high Ti contents. This effect is different from what was observed on Fe poisoned catalysts and the effects might be explained if the chemical composition of the catalyst surface is known. Therefore the catalysts were investigated by ESCA.

The catalysts were prepared by addition of 9.6 M-NaOH to an aqueous solution of RuCl_3 and TiCl_3 at 293 K inside a Parr pressure reactor. The catalysts were then used in hydrogenations of benzene to cyclohexene in 1.19 M-NaOH at 398 K. The used catalysts were washed with 0.01 M-NaOH, decanted and dried by evacuation at 293 K before ESCA analysis. The ratio Ti/Ru by ESCA is closely related to the nominal ratio as shown in Figure 1. This means that Ti and Ru are present either in one phase with no surface segregation effect or in two separate phases with comparable particle sizes. The Ti $2p_{3/2}$ core line has a constant value around 457.6-457.8 eV independent on the Ti content. The O 1s spectra, however, change drastically (Figure 2). At the highest Ti content there is a major oxygen component at 529.6 eV assigned to lattice oxygen in TiO_2 . At lower Ti contents the oxygen peak could be resolved into three peaks, one at 531.1 eV is assigned to hydroxide oxygen, one at 532.7 eV to physisorbed water and the third one to lattice oxygen in TiO_2 as above. The conclusion is that a ruthenium titanate or rather a mixed ruthenium-titanium hydrous oxide is formed.

The Ru $3d_{5/2}$ core line exhibits a continuous shift from 279.9 to 281.6 eV with increasing amount of Ti. This shift can be explained by the presence of two different ruthenium species, in differing amounts depending on the Ti content. The spectra

shown in Figure 3 have been resolved into four Gaussian components two of them representing Ru $3d_{3/2}$ and $3d_{5/2}$ for ruthenium hydrous oxide and for metallic ruthenium and the other two representing the C 1s line for carbon contamination. As the Ti content increases the amount of metallic Ru decreases. The reason is that the addition of Ti prevents the reduction of some of the ruthenium and this indicates the presence of mixed hydrous oxides.

In Figure 4 the dependence of the rate of hydrogenation on the amount of metallic ruthenium is illustrated. As shown before there is an influence of iron on the rate of hydrogenation. It was also shown that the catalyst is poisoned by iron corroded from the reactor walls. When the influence of this amount is subtracted there is a linear dependence of the rate of hydrogenation on the amount of metallic ruthenium present.

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III

HYDROGENATION OF BENZENE TO CYCLOHEXENE ON A
RUTHENIUM CATALYST: Physical and Chemical Charac-
terisation of the Catalyst and its Precursor.

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Synopsis

The chemical and physical characteristics of a ruthenium catalyst used in the hydrogenation of benzene to cyclohexene has been investigated. The active catalyst consists of metallic ruthenium obtained by hydrogen reduction of the precursor suspended in the alkaline aqueous phase. The precursor consists of hydrous oxides of ruthenium with a surface area of $27 \text{ m}^2/\text{g}$. After reduction the surface area increases to $112 \text{ m}^2/\text{g}$ and a drastic change in pore size distribution occurs. The average pore diameter decreases from 28 to 13 nm and the number of pores below 8 nm increases substantially. The macroscopic particle size, in the range 25 to 40 μm , decreases along with the decreasing ruthenium concentration. Poisoning of the catalyst by corrosion products, mainly hydroxides of iron and chromium, is also discussed.

1. Introduction

Cyclohexene has been shown to be an intermediate in the hydrogenation of benzene to cyclohexane. Different metallic catalysts have been used, but ruthenium gives by far the best yield of cyclohexene¹⁻¹². The results given in literature do not include any investigations of the structure and the chemistry of the catalyst. In two papers¹³⁻¹⁴, the influence of various reaction factors on the yield of cyclohexene and on the rate of hydrogenation of benzene were given. In these papers the authors indicated influence of mass transport processes. Important physical parameters, eg. porosity, particle diameter, pore diameter, and pore size distribution, would be needed for future mass transport calculations. In this investigation particle diameters were measured by sedimentation techniques and by microscopy. The pore size distributions were determined by adsorption of nitrogen.

To better understand the chemistry of the hydrogenation of benzene to cyclohexene, information about the surface area, the metal crystallite size and also the chemical state of the ruthenium in the catalyst are needed. The surface area was determined by the adsorption of nitrogen using the BET and the t-methods. For the determination of the crystallite size two common methods, namely electron microscopy and X-ray line broadening, were used. Finally the chemical state of the catalyst was characterised by the use of the ESCA technique.

2. Experimental

2.1 Materials

Most of the materials used have been described previously¹³⁻¹⁴. The catalyst precursor was prepared from ruthenium (III) chloride hydrate (Fluka AG, purum, 10-15% water) and sodium hydroxide (EKA, 98,6% NaOH, 0.1% Na₂CO₃ and < 0.002% metals (Al, Fe, Ag, Ca, Pb and Ni)) both dissolved in distilled water and stored under an argon atmosphere. The nitrogen gas used in the adsorption measurements was of high purity (Alfax N 52, 99.9992% N₂, <3 ppmv H₂O, <2 ppmv O₂, <2 ppmv H₂, <10 ppmv Ar, <0.5 ppmv C_nH_m and <0.5 ppmv CO) and was used as received. The reference material for the X-ray diffraction analysis was metallic ruthenium (Kebo 1.3761 puriss 99.9% Ru) and for ESCA measurements RuCl₃·3H₂O (Kebo 48.9% Ru) and (NH₄)₂RuCl₆ (Fluka AG, puriss).

2.2 Catalyst preparation

The catalyst precursors were precipitated in a double-walled glass vessel at 353 K by instantaneously adding 9.6 M-NaOH to an aqueous solution of RuCl₃ (5 g l⁻¹). The precipitation was performed under an argon atmosphere and the solution was gently stirred by a magnetic stirrer. The final concentration of NaOH was 1.19 M. The precipitate was then aged at the same temperature for one hour under a stream of argon (50 cm³ min⁻¹).

Reduction of the precursors to active catalysts were perform-

ed in a stainless steel reactor with Teflon-covered walls at 318 K, 3.6 MPa H_2 while stirring (20 rps) for one hour. Both the precursor and the reduced catalyst were subsequently washed with ten portions of 0.01 M-NaOH and dried by evacuation at room temperature (293 K) before examination. The samples used for the sedimentation analyses were precipitated at room temperature inside the stainless steel reactor and used in hydrogenations of benzene in the aqueous phase at 388 K and 3.5 MPa H_2 . They were not washed before the measurements. The samples investigated by ESCA were also precipitated in the reactor, used as catalysts in the hydrogenation of benzene, washed with diluted NaOH (pH 7-13) or concentrated HCl and subsequently transferred to the ESCA apparatus as described below.

2.3 Measurements of the total pore volume

The total pore volume was measured on a perkin-Elmer Shell Model 212 D Sorptometer. The measurements were performed by adsorbing pure nitrogen at a relative pressure of 0.98 at liquid nitrogen temperature (77 K). After the adsorption the temperature was raised and the amount of nitrogen desorbed was measured with a thermal conductivity cell and recorded on a strip chart. The amount of nitrogen desorbed per gram of catalyst was calculated from calibrated peak areas. The porosity (ϵ) was calculated from the total pore volume and the density of the solid as recommended¹⁵. The density of the ruthenium metal (12.3 g cm^{-3}) was obtained from literature¹⁶ and the density for the unreduced catalyst (3.8 g cm^{-3})

was measured by pycnometry.

2.4 Adsorption measurements

A micro-BET apparatus¹⁷ was used for measuring the adsorption isotherm of nitrogen at 77 K. The adsorbent sample was out-gassed overnight at room temperature at a pressure of 0.01 Pa. Gas pressures were measured on a mercury manometer. The time needed for adsorption equilibrium to be established was generally 15 to 30 minutes. Both the BET and the t-method were employed to calculate the surface area (S_{BET} and S_t respectively). The pore size distributions were calculated from the desorption branch using the method of Dollimore and Heal¹⁸ with the correction suggested by Emig and Hofmann¹⁹. The average pore diameter was calculated from the total pore volume and the BET area as described by Innes¹⁶.

2.5 Microscopy

The metal crystallite size was estimated from micrographs taken with a JEOL JEM 100 U transmission electron microscope (magnification 200 000). The particle size distribution of the reduced catalyst was determined from micrographs taken with a JEOL JSM-U3 scanning electron microscope (magnification 300). This microscope was equipped with an X-ray energy dispersive spectrometer which allowed for simultaneous microanalysis to be performed.

2.6. X-ray diffraction studies

X-ray diffraction patterns of the samples were recorded on a Philips PW 1310 powder diffraction unit equipped with a PW 1050 wide angle goniometer.

Using Cu K α radiation the samples were scanned over the range $2\theta=80$ to 10° . Peaks were identified by comparison with standard diffraction data²⁰. The average particle size (D) of the ruthenium crystallites was calculated from the Scherrer equation²¹; $D = K\lambda / (B^2 - b^2)^{\frac{1}{2}} \cos \theta$. The instrumental broadening (b) was determined from the peak widths of a highly crystalline sample of ruthenium metal. The peaks for the catalysts were broad and overlapping occurred for the ruthenium peaks (100), (002) and (101). The peak width used in the calculation of the crystallite size was therefore measured from peak (101) with two times the value of half the width at the higher 2θ , where the influence of overlapping is small. The value of the classical Scherrer constant (K=0.9) was used.

2.7 Sedimentation analysis

The particle sizes of catalysts used were determined by the method of fixed-position pipette incremental sedimentation²². The measurements were performed at 293 K in 1.19 M-NaOH, which is the normal hydrogenation media. The density of the falling particle (3.06 g cm^{-3}) was calculated from the density of metallic ruthenium and the measured porosity (0.82). The pores of the particle were considered to contain 1.19 M

NaOH during the sedimentation experiment.

2.8 ESCA studies

ESCA measurements were performed on an AEI ES 200B electron spectrometer equipped with an Al-anode (1486.6 eV). The analyser was operated in the fixed retarding mode and calibrated as described²³. Maximal slit widths were chosen to enhance the sensitivity. The full width at half maximum (FWHM) of the Au 4f_{7/2} line was then 1.8 eV. Oil diffusion pumps fitted with cold traps produced a vacuum around 10^{-6} Pa. Sample charging was corrected for with the Au 4f_{7/2} line (83.8 eV) by evaporating gold in appropriate amounts on selected samples. A JEE 4B vacuum evaporator was used. Charging effects were also checked for some samples with the C 1s line of carbon contamination (285.0 eV). This was carried out at a low-emission angle to increase the surface sensitivity and thereby the intensity of the carbon-contamination line²⁴. The error in the binding energy (B.E.) measurements is estimated to be ± 0.1 eV.

Quantitative ESCA analysis was performed as described by Carter et al.²⁵; their sensitivity factors of C 1s = 1, O 1s = 2.7, Ru 3d_{5/2} = 7.4, Fe 2p_{3/2} = 8.7 and Cr 2p_{3/2} = 6.7 were used. Areas were measured with a planimeter. A detailed description of the procedures is given²⁶.

Catalyst slurries were dried by evacuation directly on the sample holder (Ag-foil) in the pre-vacuum of the ESCA spectro-

meter or in a vacuum excicator. No differences in the ESCA spectra were observed for these two preparation techniques. This was true even for samples exposed to air for longer periods of time.

3. Results and Discussion

3.1 Surface area and pore structure

Adsorption isotherms for N_2 on a reduced catalyst and its precursor are given in Figure 1. Both isotherms are of type II in the BDDT classification²⁷. The precursor shows an isotherm with hysteresis above $p/p_0 = 0.6$ indicating fairly large pores. The reduced catalyst shows a much wider hysteresis loop extending down to $p/p_0 = 0.4$. This indicates a greater amount of smaller pores. The total amount of adsorbed N_2 is much higher for the reduced catalyst than for its precursor.

The pore-size distributions for the catalyst and its precursor are given in Figure 2. There is a close resemblance in the pore structure. The pore-size distribution is wide for both samples with several maxima. In the reduced catalyst all the maxima are of a similar amplitude, while in the precursor most of the pore volume is contained in pores > 4 nm width.

Calculation of the surface area by the BET- and t-methods were performed (Table 1). The surface area increases from 27 to $112 \text{ m}^2 \text{ g}^{-1}$ as a result of the reduction. In Figure 3

the volume of adsorbed N_2 is plotted against the thickness of the multilayer. The plot, which is linear at low p/p_0 , shows that both the precursor and the catalyst are compounds without micropores but with mesopores of a wide distribution indicated by the upward trend at high p/p_0 . The linear regions give surface areas, S_t , which are in good agreement with the BET areas as expected for compounds without microporosity. The values for S_{cum} from the pore-size distribution calculations are shown in Table 1 and are also in good agreement with S_{BET} . S_{cum} was calculated down to a pore radius of 1.35 nm.

Figure 4 shows the distribution of the surface area. The precursor shows a bimodal distribution with maxima around 5 and 13 nm. Conversely, the reduced catalyst has only one maximum around 3 nm. Both the absolute surface area and the surface area (%) contained in small pores are considerably smaller for the precursor than for the reduced catalyst. For the precursor the surface area (%) in pores < 4 nm is 17% compared with 47 % for the reduced catalyst. The reduction process thus opens up a large amount of small pores, thereby increasing the total surface area sharply.

3.2 Total pore volume

The results from measurements of the total pore volume and the catalyst porosity are shown in Table 1. The pore volume increases from 0.19 to $0.37 \text{ cm}^3 \text{ g}^{-1}$ as the catalyst precursor is reduced. The pore volume obtained in the pore-size distri-

bution calculations is only 0.13 and $0.31 \text{ cm}^3 \text{ g}^{-1}$ respectively. Therefore 30 and 20% of the total pore volume is contained in pores with a radius $> 20 \text{ nm}$. The porosity increases from 0.41 to 0.82 as the catalyst precursor is reduced.

The catalyst produced by reducing the hydroxide in a 1.19 M-NaOH aqueous phase at 318 K for one hour at 3.55 MPa H_2 inside the reactor thus has good characteristics: a high surface area ($110 \text{ m}^2 \text{ g}^{-1}$) and a wide distribution of pores to accomplish an easy transport of reactants and products to and from the active surface.

3.3 Particle size

The catalyst is suspended as a slurry in the alkaline aqueous phase when used in the hydrogenation of benzene to cyclohexene^{13,14}. The main factor, determining the influence of pore diffusion processes on the rate of hydrogenation, is the diameter of the particles suspended in the water phase.

Figure 5 shows SEM micrographs of the reduced catalyst and its precursor. The catalyst precursor is composed of large lumps of irregularly shaped particles probably originating from cracking of large particles during the drying process. Some particles are as large as $1200 \mu\text{m} \times 400 \mu\text{m}$, although most of them are c $250 \mu\text{m}$. Very small particles are also present. The reduced catalyst shown consists of a distribution of spherical particles with diameters in the range $10\text{-}70 \mu\text{m}$ and some rod-shaped particles c $50\text{-}100 \mu\text{m}$ long and with a

11.
diameter of 10-15 μm . The porosity is also greater for the reduced catalyst than for its precursor.

The particle-size distributions for different reduced catalysts are illustrated in Figure 6. The catalysts were precipitated from aqueous RuCl_3 solutions where the initial concentration was 0.75, 3.50 and 5.00 $\text{g dm}_{\text{aq}}^{-3}$ for samples A-C.. Sample C was measured from SEM micrographs and A and B by a sedimentation technique. The surface average diameter $d_{\text{sv}} = \sum n_i d_i^3 / \sum n_i d_i^2$ increased from 25 to 30 to 40 μm as the initial concentration was increased. The different widths of the distributions are probably due to the different techniques used.

3.4 Identification by X-ray energy dispersive analysis and X-ray diffraction

The SEM measurements also included X-ray energy dispersive analysis. The samples used in this investigation were precipitated in a glass vessel¹⁴ and subsequently reduced in a reactor with Teflon-covered walls. No corrosion products such as Fe, Ni or Cr could be detected which implies that the rate of corrosion is quite low at 318 K. Three elements were detected: Ru, Si and Ca. Both the reduced catalyst and its precursor consisted of ruthenium with small amounts of Si and Ca evenly distributed over the catalyst. Si and Ca were assumed to be dissolved from the glass vessel during the preparation procedure. The reduced catalyst, its precursor and a crystalline reference sample (99.9% Ru) were

analysed by X-ray diffraction and compared with data for metallic ruthenium²⁰. The result is shown in Figure 7 and data are presented in Table 2. Both the catalyst and its precursor exhibit broad and weak diffraction lines. This broadening of the lines is assumed to be caused by small crystallites. The precursor has only one broad peak corresponding to an interplanar distance of 0.265 nm. This peak is also present in minor amounts in the profile for the reduced catalyst as shown in Figure 7. Values for ruthenium hydroxides have not been included in the Powder Diffraction File²⁸, but chemical reasoning²⁹ suggests the presence of a hydroxide or rather a hydrous oxide of ruthenium in the catalyst precursor.

Conversely, the reduced catalyst has three distinct peaks with $d=0.235$, 0.207 , and 0.159 nm representing the (100), (101), and (102) planes of metallic ruthenium. These peaks correspond very well both in interplanar spacing and intensity ratios with data for the reference sample and data from JCPDS²⁰. Because of peak overlapping, the ruthenium (002) peak is difficult to locate in the catalyst profile. As mentioned above small amounts of a peak with an interplanar distance of 0.265 nm, representing the unreduced catalyst, is also found.

The X-ray diffraction analysis thus shows that the reduced catalyst, reduced for 1 h at 318 K and 3.55 MPa H_2 , consists of metallic ruthenium with minor amounts of hydrous oxide remaining from the precursor.

3.5 Crystallite size

The crystallite size of the precursor and the reduced catalyst were determined by two methods, from TEM micrographs and from X-ray diffraction line broadening. The results are collected in Table 3. The crystallite size of the precursor was 2 nm by TEM and 1 nm by X-ray. This latter value is rather uncertain because of the very broad peak obtained and the low ratio peak to background. The crystallite size of the reduced catalyst was 3 nm and both methods yield the same result within the precision of the measurements. Calculation of the size from S_{BET} , with the assumption of free spherical particles, yields a value of 4.4 nm. With the assumption of cubic particles with 4 surfaces exposed the size was calculated to be 2.9 nm. This value is in good agreement with the measured value.

The conclusion is that the precursor, with a crystallite size of about 2 nm, while being reduced increases in size to 3 nm which is the crystallite size of the active catalyst.

3.6 ESCA studies

The catalyst precursor is prepared by mixing RuCl_3 and NaOH aqueous solutions. Initially a black precipitate is formed which probably is a mixture of Ru(III) and Ru(IV) hydrous oxides²⁹. Ru(IV) is usually present in RuCl_3 -salts and in the aqueous solutions a slow oxidation occurs³⁰. The Ru 3d electron spectrum of the precursor is shown in Figure

8 A . The BE of Ru $3d_{5/2}$ is 281.5 eV which is close to that of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, 281.6 eV. (Figure 8B and Table 4). This indicates the presence of Ru in an oxidized state. $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ has a BE of 281.4 eV which also coincides with that of the precursor. The relatively broad peaks in spectrum A probably reflect the presence of both Ru(III) and Ru(IV) in the precursor. This is thus a mixture of the two hydrous oxides of ruthenium.

The catalyst is activated during the start-up of the hydrogenation. Because the catalysts are obtained as a suspension of black particles in strong NaOH solution, the simplest procedure of preparation for analysis was to place a portion of the slurry on the sample holder and to dry by evacuation in the pre-vacuum of the spectrometer. Any air-contact influence would then be minimized (in addition the original solvent environment was kept intact as long as possible). The result is shown in Figure 8 C. It would be easy to make a false assignment for the two peaks to originate from a highly charged Ru specie. On evaporation the NaOH, when crystallizing, will cover the catalyst particles completely. The peak at 285.0 eV is due to pump oil contamination, while the one at 290.0 eV is due to CO_3^{2-} formed by reaction of atmospheric CO_2 with NaOH within the few seconds when the sample is inserted. By scratching the surface of the solid samples the catalyst particles are uncovered, and these give spectrum D in Figure 8. Here the essential feature is the appearance of a peak at 279.9 eV due to the Ru $3d_{5/2}$ core line from the catalyst.

To obtain a clean spectra from the catalyst it is necessary to remove a major part of the NaOH. It was found that for catalyst slurries with a pH < 11, clean spectra could be obtained (Figure 8 E). Hardly any C 1s lines were detected in these samples and the slurries remained basic enough to minimize dissolution of any ruthenium hydroxides. Similar spectra were also obtained at pH 9 and 7 and the washed specimen must be identical with the working catalyst. Comparison with the BE for metallic Ru (Table 4, Figure 8 G) shows that, during the initial part of the hydrogenation, the precursor hydroxide is reduced and metallic ruthenium formed.

When the catalyst is washed with concentrated HCl the solution becomes greenish-yellow indicating the presence of $\text{RuCl}_n(\text{H}_2\text{O})_{6-n}^{3-n}$ species, probably with $n = 4$ dominating³¹, and Fe-species. The product recovered from evaporating the solvent gave a Ru $3d_{5/2}$ BE of 281.9 eV reminiscent of RuCl_3 . The Ru $3d$ spectrum of HCl-washed catalyst is given in Figure 8 F. The Ru $3d_{5/2}$ BE has decreased 0.1 eV to 279.8 eV and the FWHM by 0.2 eV to 1.7 eV. This indicates the presence of a small portion of ruthenium hydrous oxides (as also found by XRD) in the original catalyst. It dissolves on HCl-treatment. The presence of small additional peaks at higher BE could explain the above mentioned shift. It is noted that a small shift of Ru core levels on adsorption of oxygen has been reported³² (Table 4). This could contribute to the shift and broadening observed here.

In correlation to the above mentioned results, it may be of interest to observe the features in the O 1s core line. These are given in Table 4 and Figure 9. Spectrum A from the catalyst precursor is a broad peak composed of one component at 531.1 and one at 529.4 eV, characteristic of OH^- and O^{2-} respectively, and this corresponds well to a hydrous oxide. Spectrum B of the pure catalyst (pH 7) shows a similar structure which indicates the presence of a small amount of hydrous oxide. O 1s spectra for catalysts at pH > 7 (spectrum C) show an increase in the OH^- component due to the presence of NaOH (spectrum E). This also is the case for unwashed, scratched catalyst. The changes can also be concluded from the O/Ru atomic ratios given in Table 4. It is extremely difficult to make these samples cover the Ag-foil support completely and for samples with a low intensity O 1s core line, a contribution from AgO_{ads} at 531.9 eV is seen. This was the case for HCl-washed used catalysts, as seen in spectrum D. We have concluded that the oxygen species with BE 529.3 eV are removed from the catalyst on HCl washing in correspondence to the dissolution of the ruthenium hydrous oxides. If the HCl treatment is followed by washing with water or soda, the original O 1s spectrum is restored.

We have observed that the precursor is not quite stable during ESCA experiments for an extended period of time. When heating the hydrous oxide in vacuum a decomposition occurs. We have studied this by running ESCA spectra of samples at various temperatures. In Figure 10 the Ru 3d and O 1s spectra are shown together with the atomic ratios O/Ru. It is inter-

esting to note that on the Ru 3 d peaks there appears to be a continuous change from the precursor towards the metal state of the catalyst. The same peak features can be simulated by adding two pairs of Gaussian curves corresponding to the hydrous oxide and the metal respectively, in various amounts. There is thus a contribution from two phases (i.e. the metal and the hydroxide) in all spectra, but their percentages vary. The major change occurs above 473 K and at 603 K when pure metal is formed, although the O 1s spectra indicates oxygen species left at 603 K. These may be ascribed to NaOH impurities with some carbonate present, since the catalyst precursor is difficult to wash.

From hydrogenation experiments performed in a stainless steel Parr reactor¹³ it is known that corrosion products poison the catalyst. Quantitative measurements have been performed on various used Ru catalysts and some results are given in Table 5. These indicate a Fe/Cr ratio similar to that in the stainless steel. No efforts were made to measure the Ni 2p_{3/2} peak due to its very low intensity. In some hydrogenation experiments a small stainless steel plate was installed in the reactor. These plates were analysed by ESCA and from BE data it appears that both Cr and Fe of the corrosion products occur as hydroxides similar to those in the protective layer on the stainless steel surface. The great increase in Cr 2p_{3/2} intensity as compared with the data for the scratched sample is due to the protective chromium hydroxide layer formed on the steel surface. The Fe/Ru ratio from ESCA data is approximately the same as the corres-

ponding AAS values. These results suggest that the corrosion products are present as a separate phase and presumably these particles give the poisoning effect by surface and pore blocking. If Fe and Cr were exclusively adsorbed as anions on the catalyst surface, one would expect a vast discrepancy between ESCA and AAS data (since by ESCA the surface is measured and by AAS the bulk composition).

4. Conclusions

The catalyst precursor is obtained as precipitated hydrous Ru(III,IV)-oxides, which consist of particles mainly around 250 μm with a low surface area of $27 \text{ m}^2\text{g}^{-1}$. These particles are built up of crystallites of 1-2 nm diameter. The pore radius is in the range 4-16 nm with an average of 14 nm.

When the catalyst is activated by reduction in situ with H_2 , the metallic state is formed. Simultaneously, all physical factors are changed. Thus, the surface area increases to $112 \text{ m}^2\text{g}^{-1}$ and the particle diameter decreases to 10-70 μm . This is also illustrated by the large increase in porosity and total pore volume of 0.82 and 0.37 respectively compared to 0.41 and 0.19 for the precursor. The crystallite size has increased to 3 nm indicating some crystallite growth phenomena during the reduction. The pore-size distribution has also changed and in particular small pores of radius 1.5-3 nm have been formed. The average pore radius for the reduced catalyst is 6.5 nm. The concentration of RuCl_3 in the precipitation solution also has an effect on

the particle size and the number of small particles increases with lowered Ru concentration, resulting in a lowering of the average particle diameter.

The corrosion products from the stainless steel reactor have been identified in the catalyst. Fe and Cr are in a chemical state similar to that in the protective layer on the stainless steel itself. The poisoning effect is suggested to be caused by surface and pore blocking by Fe and Cr hydroxides.

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Table 1. Analysis of nitrogen adsorption data

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_t ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Average pore diameter (nm)	Porosity	S_{cum} ($\text{m}^2 \text{g}^{-1}$)	V_{cum} ($\text{cm}^3 \text{g}^{-1}$)
Precursor	27	27	0.19	28	0.41	34	0.13
Reduced catalyst	112	103	0.37	13	0.82	110	0.31

Table 2. X-ray diffraction data (intensity, interplanar spacing and indices of planes)

Catalyst precursor		Reduced catalyst		Ruthenium powder (99.9% Ru)		Data for Ru metal ²⁰		
d (nm)	I/I o	d (nm)	I/I o	d (nm)	I/I o	(h,k,l)	d (nm)	I/I o
0.265	1.00	0.265	0.15	-	-	-	-	-
-	-	0.235	0.35	0.235	0.40	100	0.234	0.40
-	-	-	-	0.214	0.35	002	0.214	0.35
-	-	0.207	1.00	0.206	1.00	101	0.206	1.00
-	-	0.159	0.09	0.158	0.18	102	0.158	0.25
-	-	-	-	0.136	0.18	110	0.135	0.25
-	-	-	-	0.122	0.22	103	0.122	0.25

Table 3. Crystallite size measurements

Sample	Crystallite size	
	X-ray	TEM
	D ₁₀₁ (nm)	D (nm)
A	3.4	3.0
B	1.0	2.0

Sample A, catalyst reduced in the aqueous phase at 318 K and 3.55 MPa H₂ for 1 hour; Sample B, catalyst precursor.

Table 4. Ru 3d_{5/2} and O 1s binding energies and half widths
(within parenthesis) and O/Ru atomic ratios for some
Ru-catalysts and reference compounds.

<u>Samples</u>	<u>Ru 3d_{5/2} (eV)</u>	<u>O 1s (eV)</u>	<u>O/Ru^a</u>	<u>Ref.</u>
Catalyst Precursor	281.5 (2.5)	531.1-529.4	2.0-1.5	
RuCl ₃ ·3H ₂ O	281.6 (2.0)			
(NH ₄) RuCl ₆	283.1 (1.5)			
NaOH		531.1		
Catalyst, used ^b (Washed pH 11-7 and unwashed, scratched)	279.9 (1.9)	531.2-529.3	2.0-1.2 (pH 11) 1.1-1.0 (pH 7)	
Catalysts, used ^b (Washed conc. HCl)	279.8 (1.7)			
Ru ^O -powder (400°C, vac, 1h)	279.8 (1.8)			
Ru (001), O _{ads} , θ ≈ 0	279.9	529.8		(32)
"-"-"-, θ = 1	280.2	529.7		"
Ru ^O	280.0			(33)
RuO ₂	280.7	529.4		"
RuO ₃	282.5	530.7		"
RuO ₄	283.3	530.5-529.3		"
RuO ₂ ·xH ₂ O	281.4	530.5-529.3		"

^a O/Ru is given for the two O 1s peaks. The scatter in O/Ru ratios was ±0.5.

^b Similar results were obtained for over 15 different batches.

Table 5. Atomic ratios and BE for some elements identified
in used Ru catalysts and some reference samples.

<u>Sample</u>	<u>Ru</u>	<u>Fe</u>	<u>Cr</u>	<u>Fe 2p_{3/2}</u>	<u>Cr 2p_{3/2}</u>
<u>Ru catalysts</u>					
By ESCA	17-28	3-5	1	710.2	575.8
By AAS	22-39	5-9	1		
<u>Stainless steel^a</u>					
Scratched	-	2.7	1	709.5-706.4	576.0-573.5
After hydrogenation experiment ^b	0.88	0.15	1	710.1	576.1
Bulk data (AISI 316)	-	3.5	1		

^a SIS 2343 with a composition very similar to the reactor material AISI 316 was used.

^b A piece of stainless steel was inserted in the reactor and kept there during a normal hydrogenation experiment.

Figure text

Figure 1

Nitrogen isotherms for the reduced catalyst (A) and its precursor (B).

Figure 2

Pore-size distributions for the reduced catalyst (A) and its precursor (B).

Figure 3

t-Plot for the reduced catalyst (A) and its precursor (B).

Figure 4

Distribution of surface area as a function of the pore radius for the reduced catalyst (A) and its precursor (B).

Figure 5

SEM micrographs of the reduced catalyst (A) and its precursor (B).

Figure 6

Particle-size distributions for reduced catalysts determined by sedimentation techniques (A,B) and from SEM micrographs (C). Initial concentration of RuCl_3 was 0.75, 3.50 and 5.00 g dm⁻³_{aq} for A-C.

Figure 7

X-Ray diffraction profiles of the reduced catalyst (A), ruthenium powder (B) and the precursor (C).

Figure 8

Ru 3d binding energy region of electron spectra for some Ru catalysts and reference samples.

A. Catalyst precursor

B. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$

C. Used catalysts. Dried in original solution (pH 14).

D. Same samples as in C, followed by scratching.

E. Used catalysts. Washed (pH 11, 9 or 7).

F. Used catalysts. Washed with conc. HCl.

G. Ru powder. Heated at 673 K for 1 h in vacuum.

Figure 9

O 1s electron spectra for some Ru catalysts and reference samples.

A. Catalyst precursor

B. Used catalysts. Washed (pH 7).

C. Used catalysts. Washed (pH 11).

D. Used catalysts. Washed with conc. HCl.

E. NaOH

Figure 10

Ru 3d and O 1s electron spectra for catalyst precursor heated in vacuum at varying temperatures (K) and atomic ratios O/Ru.

A 298, 3.5/1; B 473, 3.7/1; C 573, 1.7/1; D 603, 1.2/1

Figure 1

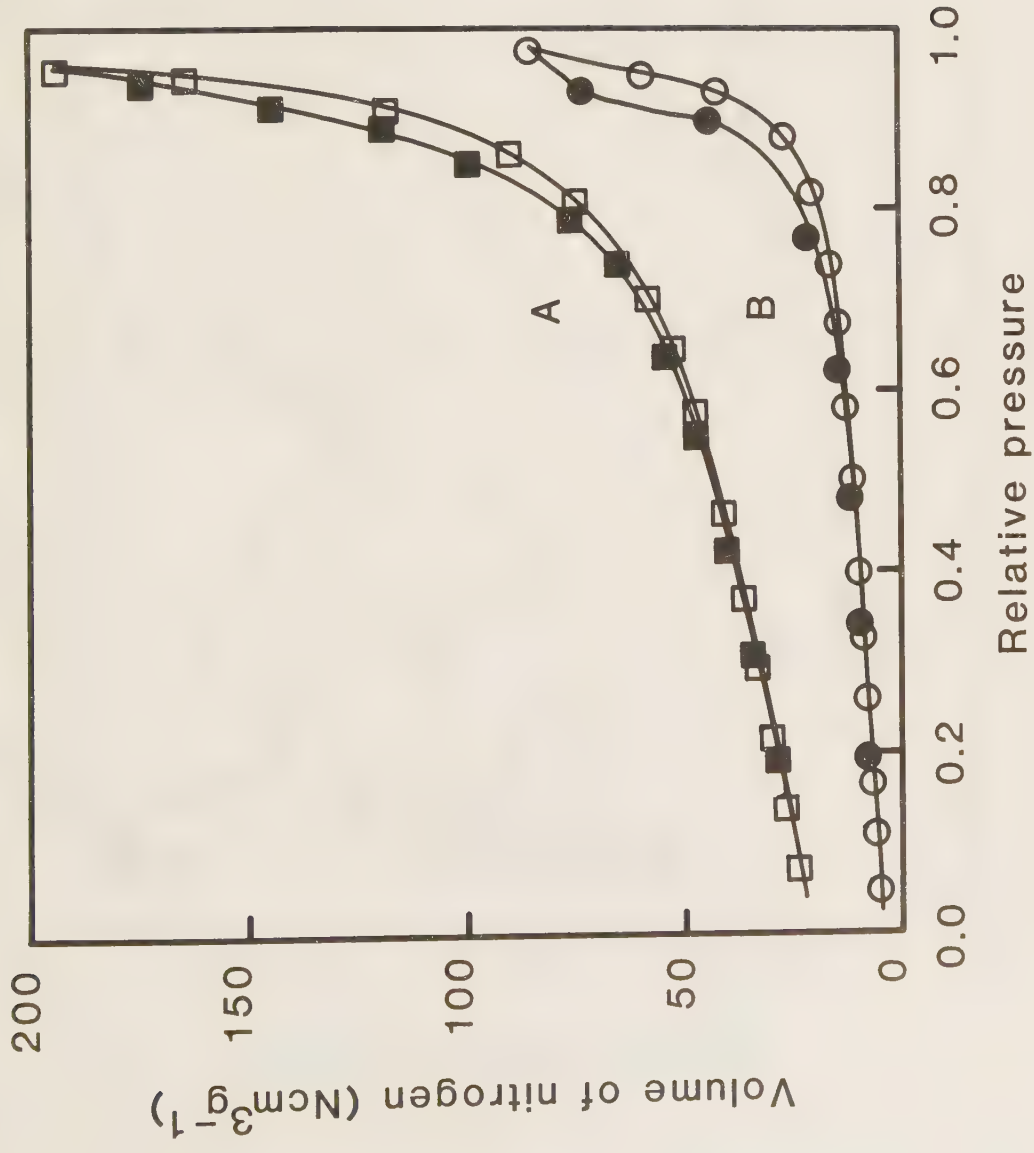
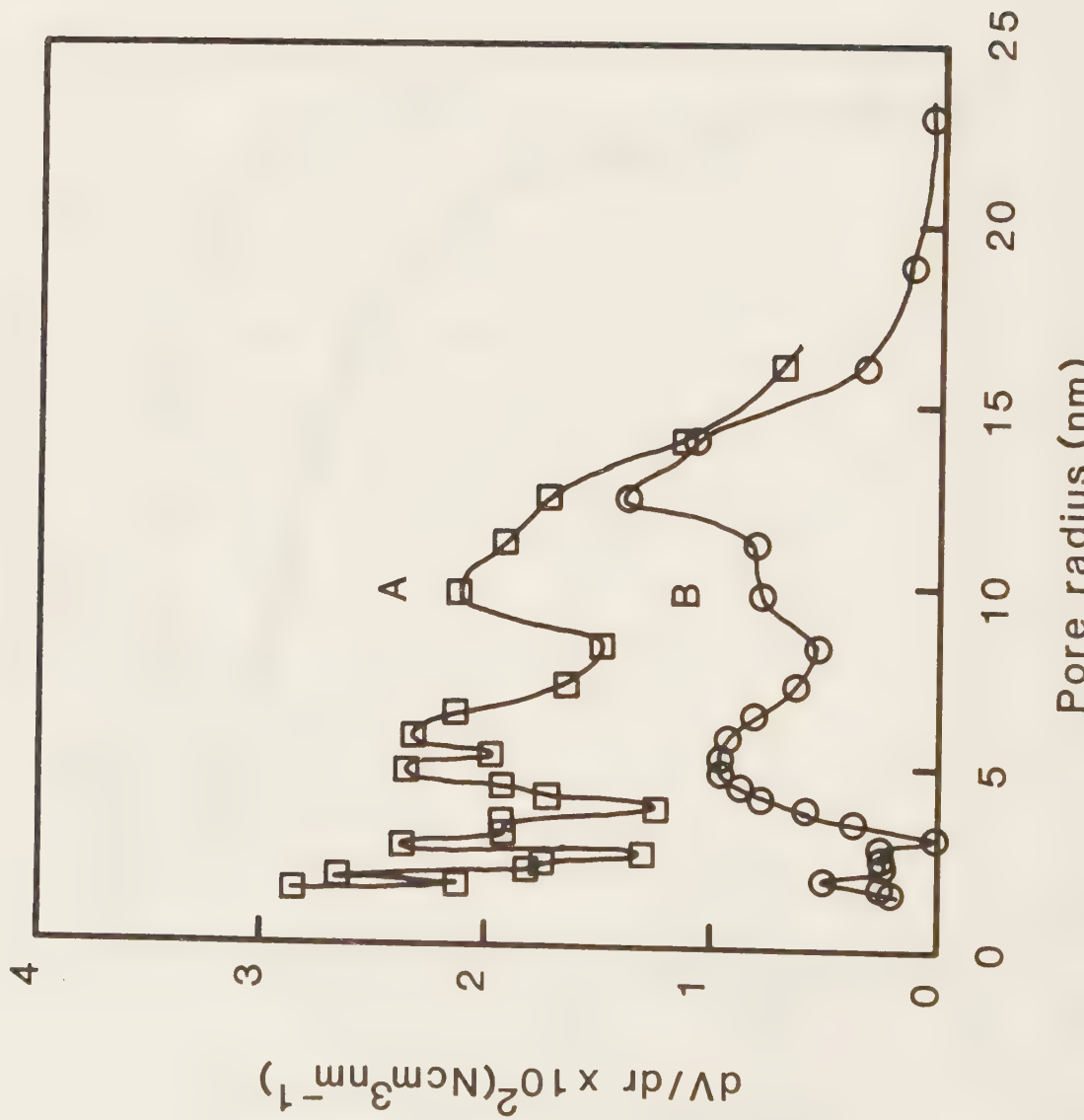


Figure 2



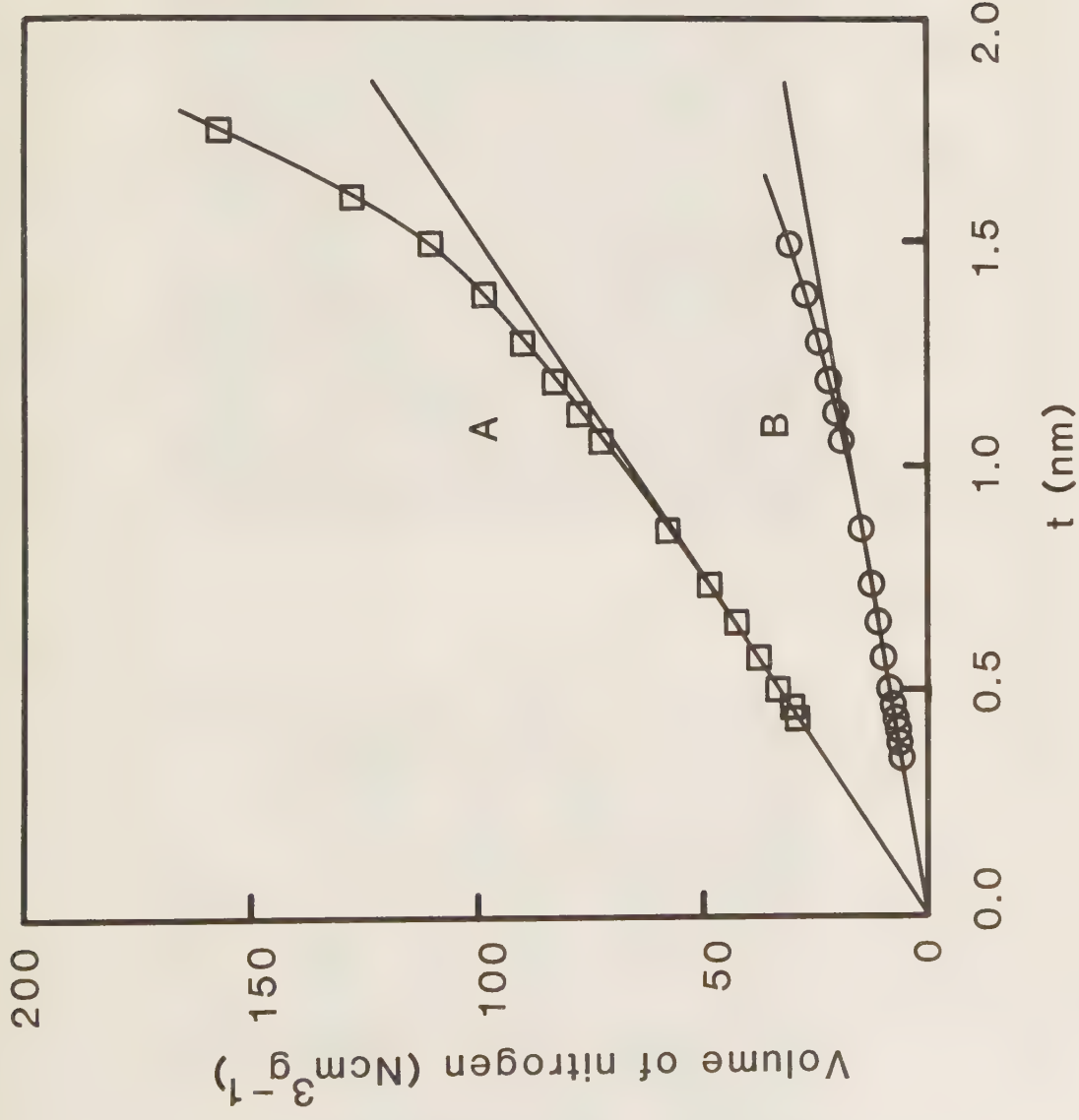


Figure 3

Figure 4

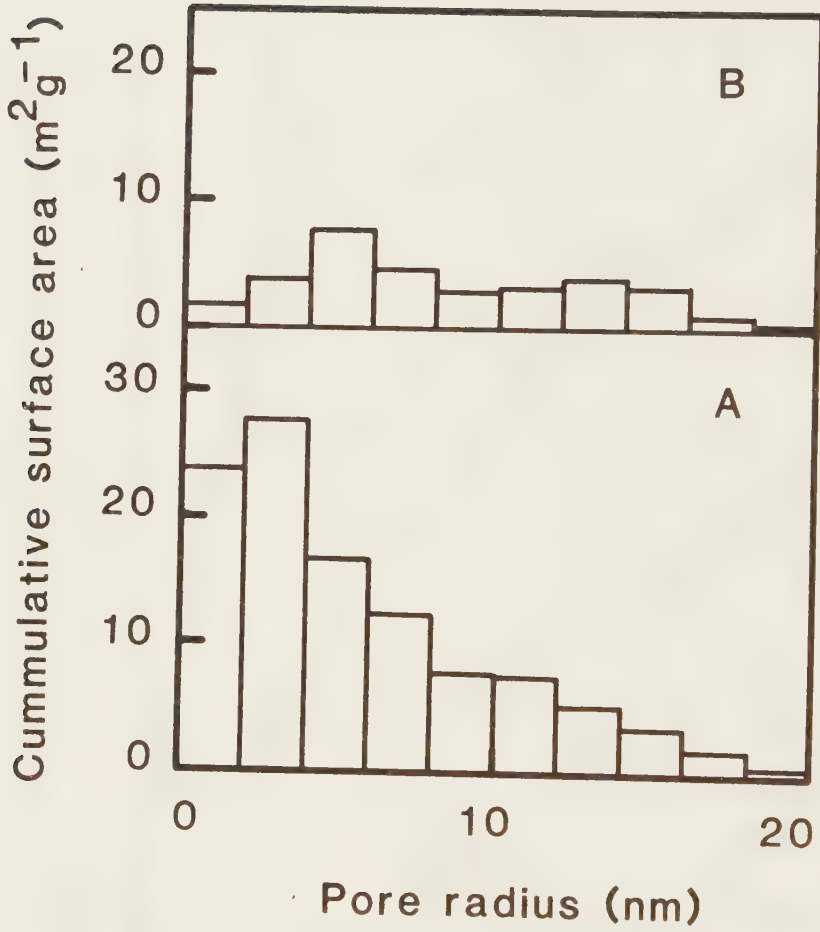
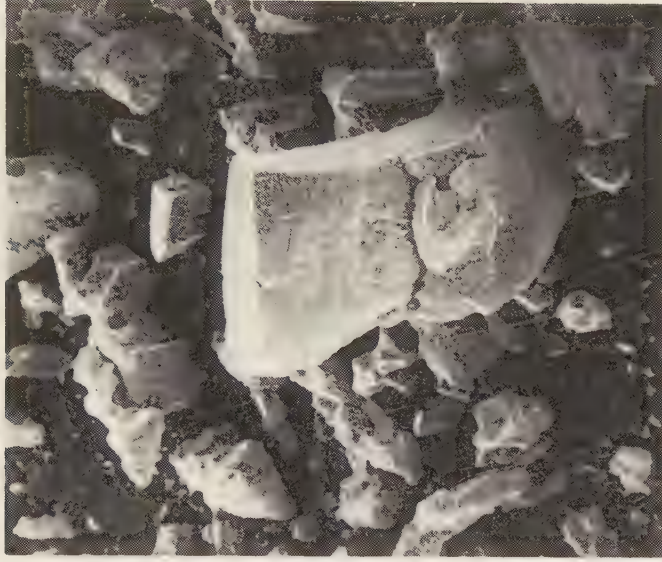


Figure 5



A

40 μm



B

200 μm

Figure 6

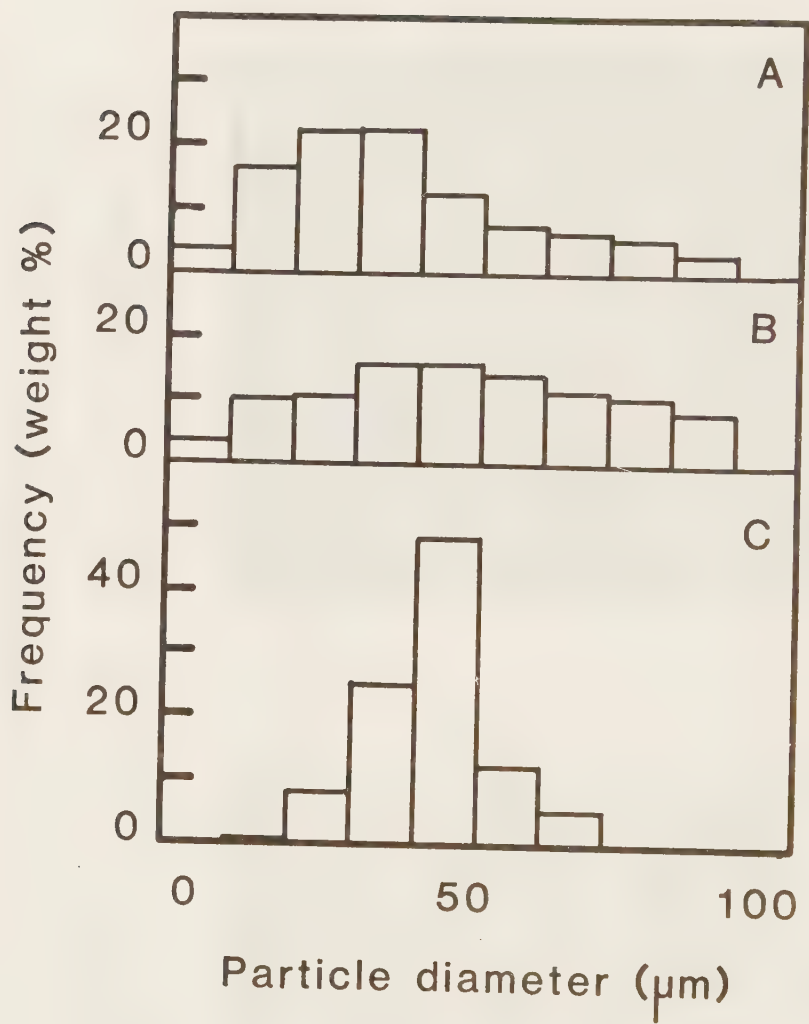


Figure 7

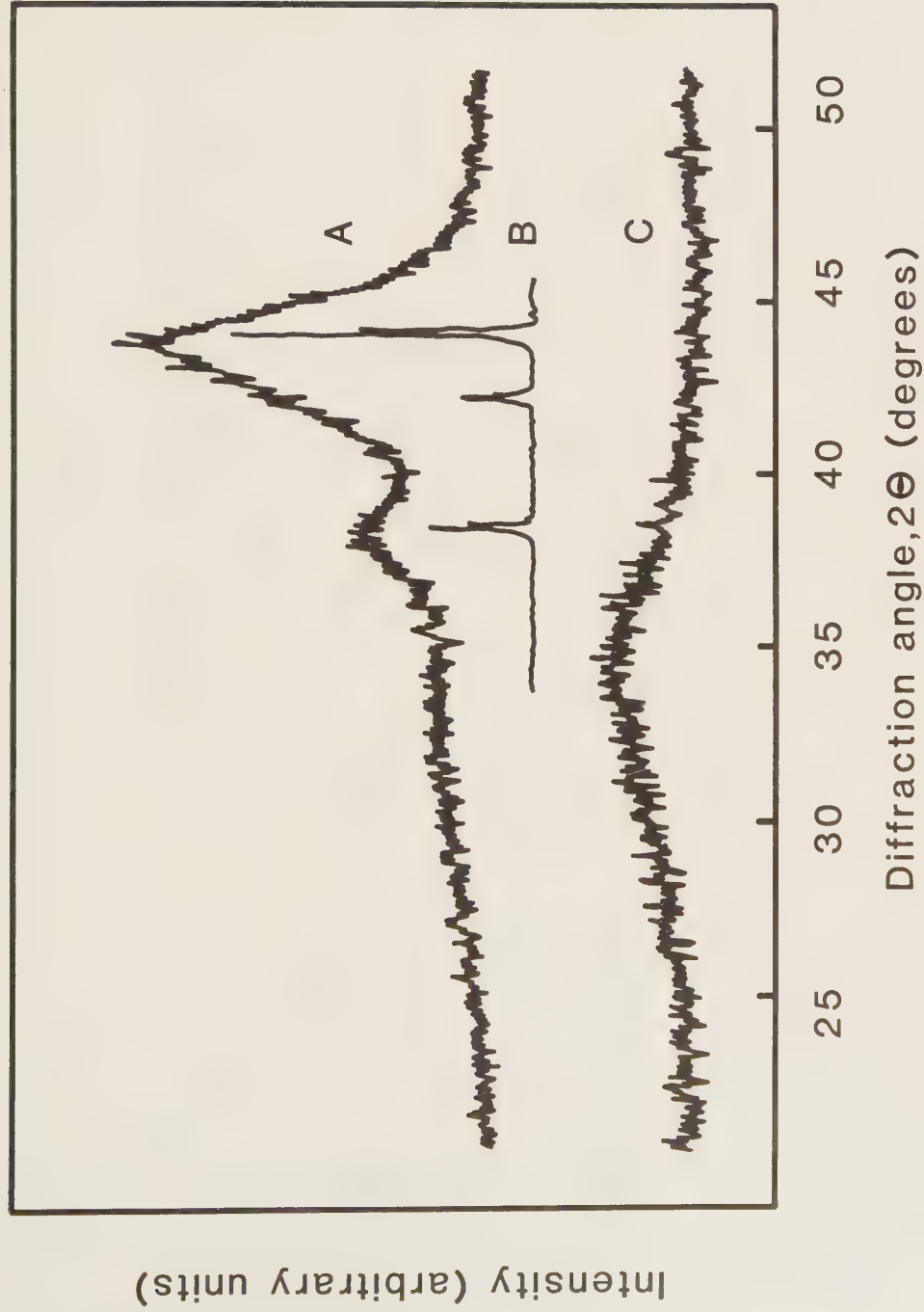


Figure 8

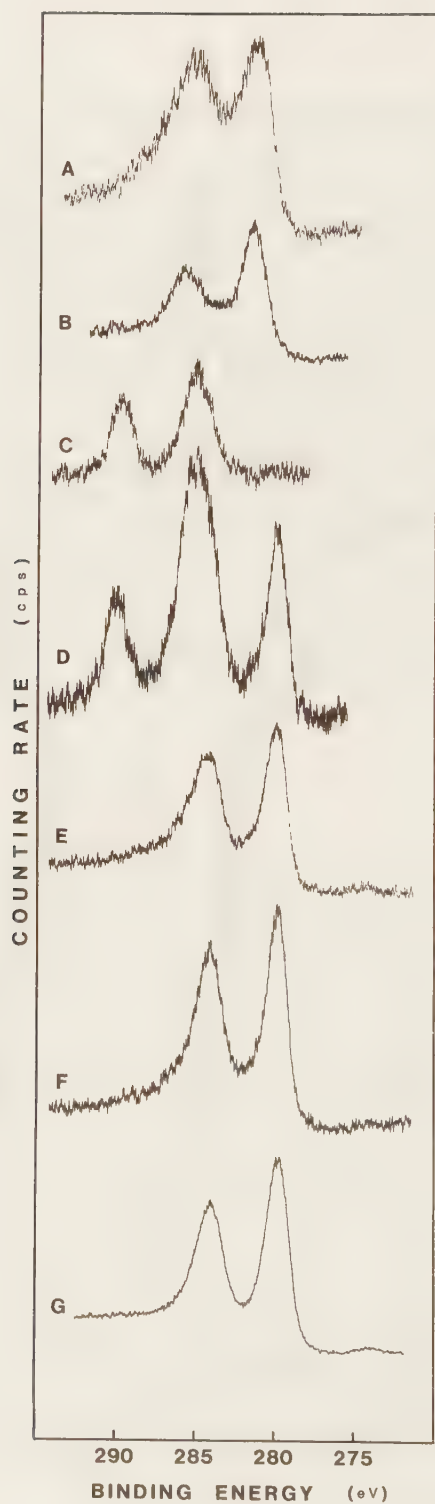


Figure 9

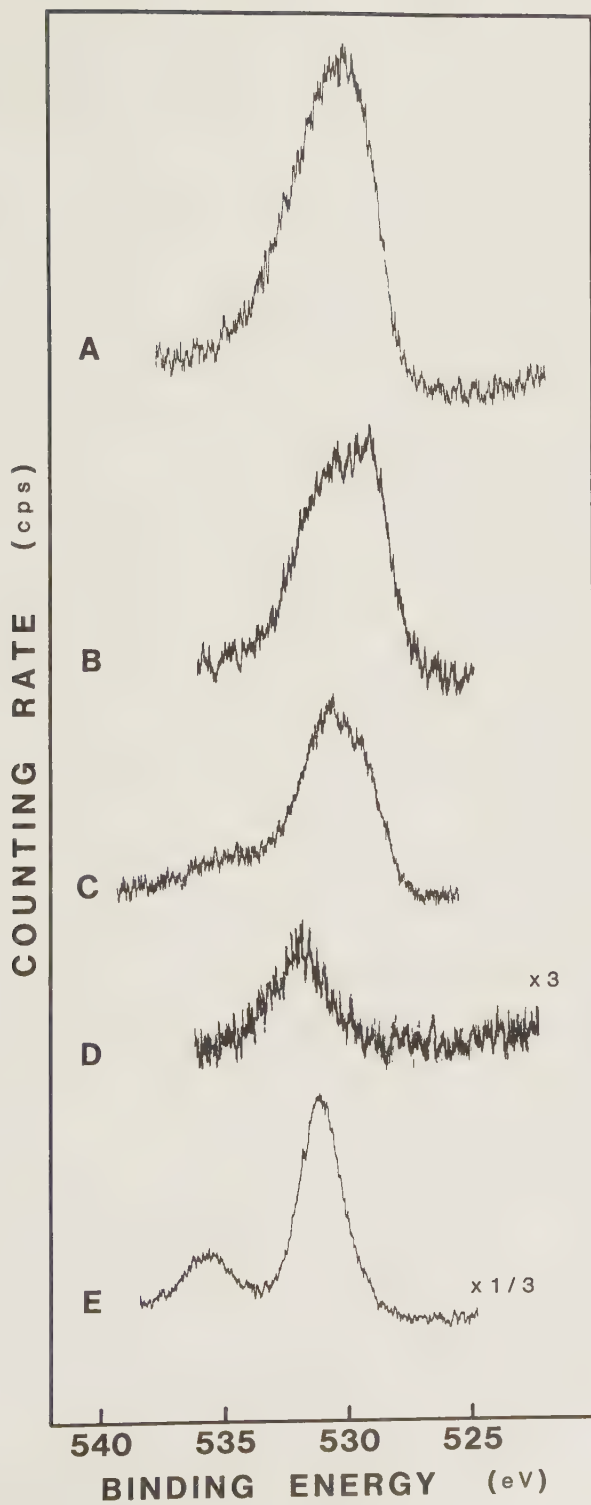
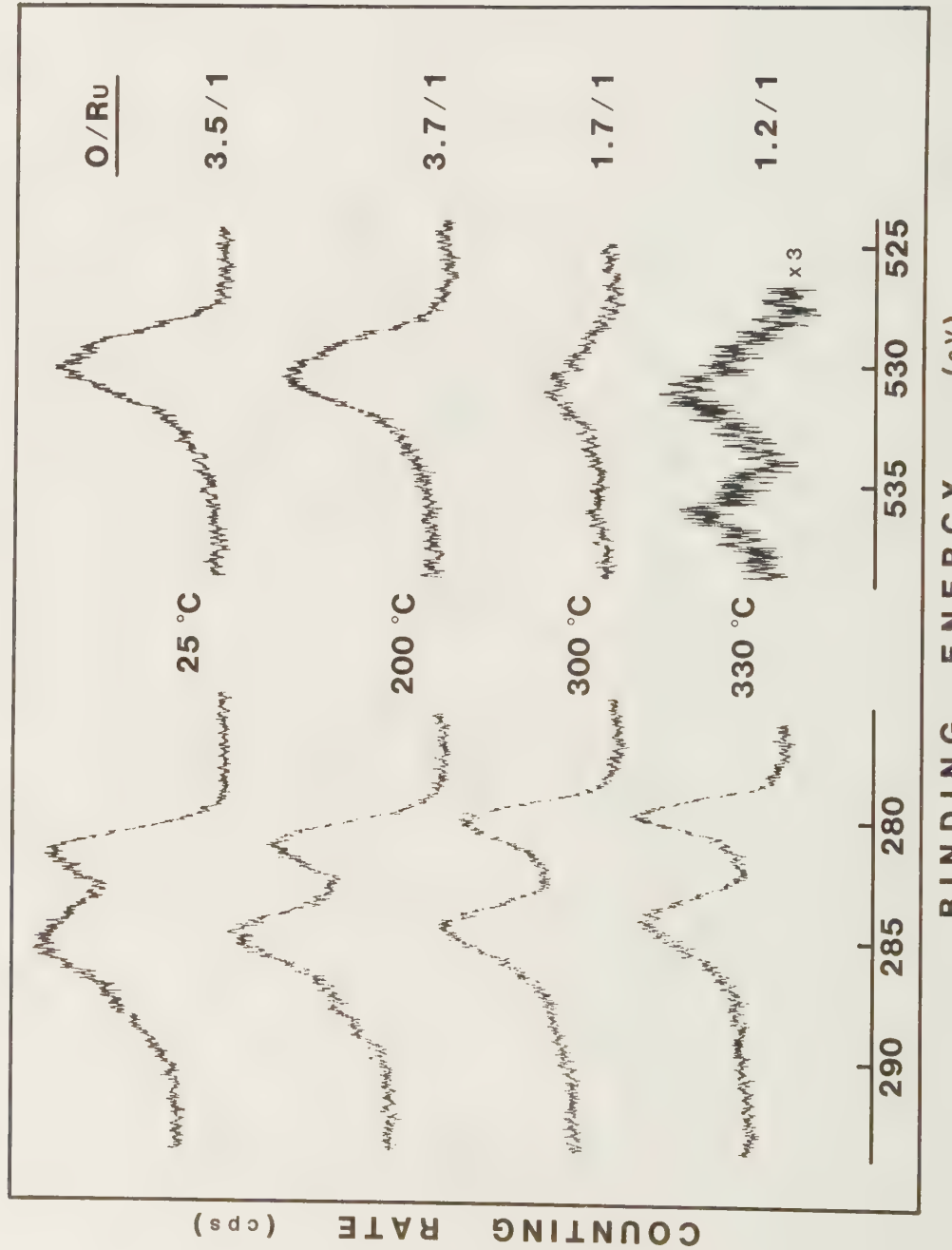


Figure 10



IV

HYDROGENATION OF BENZENE TO CYCLOHEXENE ON AN
UNSUPPORTED RUTHENIUM CATALYST: Physical and
Chemical Characterisation of Iron Poisoned
Catalysts in Relation to their Catalytic Per-
formance.

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Synopsis

The physical and chemical characteristics of an unsupported Fe-Ru catalyst, used in the hydrogenation of benzene to cyclohexene, has been investigated. The chemical composition was determined by XRD and ESCA. The catalyst consists of an Fe-Ru alloy and iron hydrous oxides. The texture of the catalyst was determined by adsorption measurements and by microscopy. On increased iron content the BET surface area and the pore volume decreases. The decrease in surface area is uniform affecting all pore size intervals. The surface area measured by adsorption of hydrogen decreases more rapidly than the BET surface area. The macroscopic particle size is constant up to an iron content of 15-20%. At higher contents their size decreases rapidly.

The decreased hydrogen coverage on the catalyst surface on addition of iron was correlated to an increased yield of the desired intermediate cyclohexene. The chemisorption of benzene is also decreased by iron and at poisoning levels above the optimal, planar adsorption of benzene is probably sterically hindered, while cyclohexene adsorption is less affected. This results in a decreased yield of cyclohexene at iron contents above the optimal one.

The hydrogenation of benzene to cyclohexene performed in an alkaline aqueous phase is shown to be influenced by diffusion processes. The catalyst particles, 6-14 μm diameter, are large enough to make the overall rate limited by pore diffusion pro-

cesses at 390 K. The maximum yield of cyclohexene has been correlated to the calculated effectiveness factor. The influence of poisoning and mass transfer, on the process, has been separated.

1. Introduction

Increased interest has recently been shown in ruthenium as a catalyst for the selective hydrogenation of benzene to cyclohexene¹⁻⁶. High yields of cyclohexene are obtained when the hydrogenation of benzene is performed in an alkaline aqueous phase on ruthenium catalysts^{1,2}. Many reaction factors influence both the yield of cyclohexene and the rate of hydrogenation. Addition of poisonous species, e.g. iron, decreases the rate of hydrogenation. However, the yield of cyclohexene is quite improved and at the optimal iron content², the yield is twice as high as on pure Ru-catalysts.

Since iron additions have such a pronounced positive effect on the yield of cyclohexene, it would be interesting to correlate the changes in physical and chemical characteristics of the catalyst to the changes in yield. The chemistry and texture of pure unsupported Ru catalysts, used in the hydrogenation of benzene to cyclohexene, have been examined earlier⁷. In the present work we have extended these studies to a characterization of some iron poisoned catalysts.

The yield of the intermediate cyclohexene is expected to be influenced by poisoning of the catalyst surface, but also by

influence of pore diffusion. The effect of the poisoning can be due to blocking of certain active sites, or direct changes in the active sites by geometric or electronic means. Therefore analysis by X-ray diffraction and ESCA were performed to investigate the phases that are present in the iron poisoned catalysts.

The rate of hydrogenation may also be affected by similar factors as the yield, but more plausible is a direct decrease of the active surface area with increasing iron additions. These factors have been investigated by volumetric measurements of N_2 and H_2 adsorption.

Pore diffusion limitations for consecutive reactions normally result in a decrease in the yield of the intermediate. It has been mentioned and showed before^{1,2} that the hydrogenation of benzene to cyclohexene in the aqueous phase is somewhat limited by diffusion of hydrogen through the liquid film around the gas bubble. Since this diffusion effect exists, it is probable that pore diffusion effects are important too. The decisive parameter for mass transport properties is the macroscopic catalyst particle size, which may be influenced by the iron additions. Therefore we have measured the particle diameter by microscopy. When the particle size is known, effectiveness factors can be calculated and the influence on the yield of cyclohexene evaluated. A secondary effect of the iron additions may be an influence on effective diffusivities if the catalyst pore system is changed. Therefore the pore size distributions as a function of the iron content have been studied by volumetric measurements of N_2 adsorption.

2. Experimental

2.1 Materials

The materials used were ruthenium(III) chloride hydrate (Fluka AG, purum, 10-15% water), iron(II) sulphate heptahydrate (Merck Pro Analyysi >99,5%), iron(III) chloride hexahydrate (Merck Pro Analyysi >99%) and sodium hydroxide (EKA >98.6%). Reference materials for ESCA measurements were Fe-foil (MRC, marz grade 99.99%), Fe_2O_3 (Mallinchrodt, Analytical Reagent), Fe_3O_4 (BDH, Analytical Reagent) and $\text{FeO}(\text{OH})$, synthesized by oxidation of an aqueous $\text{Fe}(\text{II})$ -solution.

2.2 Catalyst preparation

The catalyst precursors were precipitated in a glass vessel at 353 K by instantaneous addition of 9.6 M NaOH to an aqueous solution of ruthenium(III) chloride and ferrous sulphate or ferric chloride. The amount of poison added is presented as atom % iron ($\frac{\text{Fe} \cdot 100}{\text{Fe} + \text{Ru}}$) unless otherwise stated.

The final concentration of NaOH was 1.19 M and the precipitation was performed under an argon atmosphere. The aqueous solution was gently stirred by a magnetic stirrer during the precipitation. The precursors were subsequently pre-reduced - aged - at the same temperature in the aqueous phase for one hour with a hydrogen flow of $50 \text{ cm}^3 \text{ min}^{-1}$.

The reduction of the precursors to active catalysts was performed in the aqueous phase inside the reactor² at 3.5

MPa H_2 . The catalysts used in the adsorption measurements were reduced for one hour at 318 or 373 K, washed with 10 portions of 0.01 M NaOH and dried by evacuation at room temperature. The dried catalysts were stored under argon until needed. The catalysts used for the particle size determination were first used in normal hydrogenations at 390 K and 3.3 MPa H_2 and were stored in their mother liquor at room temperature until examined.

The samples investigated by ESCA were precipitated in the reactor, used as catalysts in the hydrogenation of benzene, washed with diluted NaOH (pH 7-13) or concentrated HCl and subsequently transferred to the ESCA apparatus as described below.

2.3 ESCA studies

The procedure for the ESCA measurements has been described elsewhere⁷. They were performed on an AEI ES200B electron spectrometer, equipped with an Al-anode (1486,6 eV). The full width at half maximum (FWHM) of the Au 4f_{7/2} line was 1.8 eV. Sample charging was corrected for by placing the Au 4f_{7/2} line at 83.8 eV. The accuracy in the B.E. determinations is estimated to ± 0.2 eV.

In the quantitative ESCA analysis - as described elsewhere⁷ - the sensitivity factors were C 1s = 1, O 1s = 2.7, Ru 3d_{5/2} = 7.4 and Fe 2p_{3/2} = 8.7. The difficulties in estimating the area of the Fe 2p_{3/2} line lies in the inherent increase in background at the high B.E. side. The background was simply

estimated as a straight line from higher to lower B.E. side of the peak. The resolution in two components was done by mirror-reflecting the low B.E. side of the peak and subtracting that component from the original peak. The fact that all quantitative data show satisfactory correlations supports the use of this method. The error in the quantitative measurements are estimated to less than 15 %.

Some spectra were digitized and smoothed⁸ on a Tektronix 4051 with a 4662 interactive digital plotter. A quadratic smooth over a number of points taken as $0.7 \times (\text{FWHM})$ were used. End points which normally are lost were estimated with a linear least squares fit⁹.

The catalyst slurries were dried by evacuation directly on the Al boat-shaped sample holder in a vacuum excicator. This procedure was found earlier to be quite satisfactory⁷. Dry samples were pressed into the same type of holders with a spatula. Some Fe-containing catalysts were kept under argon, placed on the sample holder and introduced into the spectrometer entrance lock under flowing argon with the help of a glass vessel device.

2.4 Characterisation by other techniques

Nitrogen adsorption measurements, total pore volume, porosity and pore size distributions were determined as described elsewhere⁷. Some surface area measurements were also performed on a Ströhlein areameter. Hydrogen adsorption was performed at 298 K in a micro-BET apparatus. The samples were

first degassed at 294 K for two hours at a pressure of 0.01 Pa. Then the surface area, S_{BET} , was measured by the adsorption of nitrogen at 77 K. After another degassing period hydrogen was admitted to a pressure of 60 kPa and adsorption was continued for at least 18 hours. This procedure was repeated once and finally a hydrogen adsorption-desorption isotherm was measured. The desorption isotherm behaved according to the Langmuir isotherm for dissociative adsorption and metallic surface areas and crystallite sizes were calculated from plots of the linearised form of the equation¹⁰. The BET surface area was measured after H_2 adsorption as well.

The macroscopic particle size was determined from micrographs obtained on a Leitz Elvar stereo microscope. The samples, which were first used in the hydrogenation of benzene in the aqueous phase, were normally stored in their mother liquor for 14 days before examination. Some samples were also examined directly in the course of the hydrogenation experiment. The catalyst particles were dispersed by vigorously shaking the container for 2 minutes and the particles were subsequently transferred to the microscope. At least 500 particles from several photographs taken at different locations within the drop were measured. Some particle size distributions were also obtained from SEM micrographs.

X-ray diffraction studies were performed with the same equipment as before⁷ on dried catalysts which had been passivated by addition of a 9% solution of paraffin in hexane followed by drying at room temperature in air. Sintering was

observed on samples where the passivation procedure had not been applied. The accuracy in the XRD measurements is ± 0.01 degree 2θ .

3. Results and discussion

3.1 Characterisation by X-ray diffraction

All the catalysts examined by X-ray diffraction were reduced in the aqueous phase and dried by evacuation. Some results are presented in Figure 1. All catalysts coprecipitated from RuCl_3 and FeSO_4 with an iron content of 30% or below show a pattern from ruthenium metal¹¹ only. Spectrum B, 30% iron, is a typical example where 6 peaks are clearly visible while two more in fact are present but are disguised by overlapping of neighbouring peaks.

The catalyst shown in spectrum A, 60% iron, is composed of both magnetite (Fe_3O_4) and metallic ruthenium. The magnetite peaks are marked with $\square$ and the nonoverlapping ones are in good agreement with standard diffraction data¹². At least three peaks corresponding to metallic ruthenium are also visible. The peaks due to Fe_3O_4 are not as broad as those due to ruthenium. In fact the crystallite size for Fe_3O_4 was estimated as 16.2 nm and for metallic ruthenium as 3.1 nm. Some of the iron in the catalysts made by coprecipitation of RuCl_3 and FeSO_4 is thus shown to be in the form of magnetite during the hydrogenation experiment.

Spectrum C was obtained from an unpoisoned catalyst exposed to air. This resulted in the formation of a bulk ruthenium oxide but also in a sintering of the metallic ruthenium particles. The peaks marked with ● represent the three strongest reflections of RuO_2 ¹³. The other peaks all represent metallic ruthenium with a crystallite size of around 12 nm. The crystallite size of the oxide particles is around 10 nm.

Spectrum D shows a catalyst made by coprecipitation of RuCl_3 and FeCl_3 and after exposure to air it consists of metallic ruthenium and goethite, $\alpha\text{-FeO(OH)}$ ¹⁴. The peaks marked with o represent $\alpha\text{-FeO(OH)}$ with a crystallite size of 62 nm. Two very broad and weak peaks are also present. One is the Ru (101) reflection and the other one could be ruthenium hydroxide remaining from the precursor. The ruthenium peaks gives (with considerable uncertainty) a crystallite size of 2.5 nm. The X-ray diffraction pattern for the same catalyst before sintering shows peaks from ruthenium metal only. The peaks are very weak and broad and the crystallite size is estimated to be 2.8 nm. The sintering in this case seems to affect only the iron oxide crystallites, the ruthenium ones remaining unchanged. The amount of iron in the catalyst has an effect on the sintering behaviour. When no iron is added and the catalyst is exposed to air, sintering of the metallic ruthenium particles occurs as shown in spectrum C, Figure 1. A bulk oxide, RuO_2 also appears. Slow admission of oxygen to a 10% Fe-Ru catalyst resulted in a sintering of the metallic particles, which was observed both as a twofold decrease in surface area, S_{BET} , and in a doubling of the crystallite size of the

metallic ruthenium particles. No bulk RuO_2 was observed in this case. At immediate oxygen exposure, the metallic ruthenium particles in a 20% Fe-Ru catalyst sinter and peaks from bulk RuO_2 appear in the spectra. No iron oxide peaks are visible. Finally in the presence of 40% iron, or more, the small ruthenium particles are not sintered whereas in the FeCl_3 preparation the $\alpha\text{-FeO(OH)}$ particles are (Spectrum D). The iron is thus shown to have a stabilizing effect on small ruthenium particles. This effect has been observed before on Fe-Ru/ SiO_2 catalysts¹⁵.

All these investigations have been performed on catalysts which have not been used in hydrogenation. Some X-ray diffraction analysis have also been performed on 15% Fe-Ru used catalysts. Both FeSO_4 and FeCl_3 preparations show peaks from Ru metal only as observed for the unused catalyst. Further experimentation also revealed that catalysts prepared from RuCl_3 and FeSO_4 always contained Fe_3O_4 while the ones prepared from RuCl_3 and FeCl_3 or $\text{Fe(NO}_3)_3$ contained $\alpha\text{-FeO(OH)}$.

3.2 Crystallite size and interplanar spacing

The dependence of the Ru crystallite size on the amount of ferrous sulphate was investigated by X-ray line broadening techniques⁷. Figure 2 illustrates the crystallite size of the metallic ruthenium particles which decreases from 4.0 to 3.1 nm as the amount of iron increases to 60%. In this figure a value obtained by adsorption of hydrogen is also shown. This value is slightly higher. Since X-ray methods

measure the volume average diameter and H_2 adsorption measures the surface average diameter, the former one should be larger. Our results do not agree with this fact but can be explained if strain and faulting are contributing to the X-ray line broadening. An estimate of this contribution¹⁶ yields a crystallite size of 4.3 nm at the addition of 20% iron which is 0.7 nm larger than the uncorrected value of 3.6 nm, and close to the hydrogen adsorption value for 100% Ru. The increased line broadening with increasing addition of iron may then be explained by an increased amount of strain and faulting caused by the iron inserted into the ruthenium matrix.

Figure 3 shows the interplanar spacing which decreases linearly with the percentage of iron up to 30% and remains constant at higher additions. The linear dependence indicates the formation of an alloy between Ru and Fe. FeRu alloy formation in a catalyst prepared in an aqueous phase under conditions yielding a catalyst with a surface area of $7-15 \text{ m}^2 \text{ g}^{-1}$ has been discussed earlier¹⁷. It is also known that iron and ruthenium form solid solutions with iron substituted into the ruthenium lattice for the whole concentration range studied here¹⁸. However, it should be noted that the catalysts studied here have been heated up to only 373 K at the most. According to literature data¹⁹, the lattice constant for ruthenium alloyed with iron decreases in a linear way with the amount of iron in the alloy. The amount of the iron added which is alloyed to ruthenium could be estimated as 34% by comparing the slopes of interplanar spacings versus atom % iron for the investigated catalysts and literature values for Fe-Ru bulk alloys. All

these findings support our results which imply that a part of the iron in the catalyst is alloyed to ruthenium. The other part is present as oxides, but is only detected by XRD at iron contents higher than 30%.

3.3 ESCA studies

It was shown earlier⁷ that the catalyst must be removed from the strong base solution before ESCA analysis is performed. This was satisfactorily carried out by washing with NaOH solutions of pH 11, but pure water was also used. XRD data presented here shows that vacuum dried freshly prepared Ru and Fe-Ru catalysts are oxidized and sintered, although to a limited extent, upon immediate exposure to oxygen. The catalysts used in the ESCA investigation are, however, used in hydrogenations and thereafter washed before analysis. These are probably passivated during washing or are more likely already passivated in the hydrogenation mixture.

All catalysts were used in hydrogenation in the Teflon covered stainless steel reactor. The Teflon greatly reduces the dissolution of iron from the reactor material. ESCA analysis of five samples showed an Fe/Ru atom ratio of ≈ 0.03 . This low amount has a negligible influence on the activity².

In all catalysts studied ruthenium was found to be in the metallic state. Since this was earlier reported to be the case also for pure ruthenium catalysts⁷ we will here concentrate on the state of the iron added.

Binding energies and half widths of the Fe $2p_{3/2}$ and O 1s core lines are given in Table 1 for the Ru-Fe catalysts and some reference compounds. See also Figures 4 and 5. It is evident that in the used catalysts iron is present in both an oxidized and a metallic state. Experiments were performed where samples were handled and inserted into the spectrometer under argon, but no difference compared with the ordinary treatment was observed. Considering the stability diagrams given by Pourbaix²⁰, it seems unlikely that a complete conversion to metallic iron occurs during the hydrogenation conditions used. This is also concluded from results on Fe/TiO₂ catalysts²¹. A more severe hydrogen reduction at 673 K for 4 hours resulted in a complete conversion of all iron to the metallic state in Fe-Ru catalysts²². Alloy formation was also discussed for these catalysts¹⁷. The formation of bimetallic Fe-Ru particles has been observed for silicagel²³ and NaY²⁴ supported catalysts, although these were also prepared in a different way.

Therefore, we suggest that the catalyst in use contain metallic ruthenium and iron as well as iron hydrous oxides. The XRD measurements revealed, for the concentration ranges used in the hydrogenations, only the presence of metallic ruthenium. Therefore, the oxidized iron must be present in an amorphous form, while the metallic iron - as suggested earlier - is alloyed to the ruthenium metal. Any assignments of the ESCA data for the oxidized iron to one compound exclusively seems impossible considering the close resemblance between the Fe $2p_{3/2}$ -lines for the various compounds as given in Figure 4.

In Figure 5 the O 1s spectra are given. From a comparison between samples containing low and high amounts of iron, a difference in the O 1s line is apparent. According to the difference spectra this component has a B.E. around 530 eV, which would suggest the presence of Fe_3O_4 or $\alpha\text{-FeO(OH)}$. In Figure 6 the atom ratio O/Ru versus atom ratio Fe/Ru, both obtained from ESCA analysis, are given. Although there is a substantial scatter in the data it is revealed that an increase in the iron content is associated with an increase in the oxygen content, this evidently being due to the presence of iron hydrous oxides. One interesting observation is that extrapolation to zero iron content suggests a O/Ru atom ratio of 0.7-1 for the pure Ru-catalyst. The O/Ru ratio for bulk Ru-hydroxide is 3.5. A catalyst covered by a monolayer of hydroxide would yield an intensity approximately 30% of the former one, corresponding to $\text{O/Ru} \approx 1$ as observed.

The coprecipitated catalysts were prepared from two different solutions of iron(II)sulphate in distilled water. One (A) was a stock solution and the other (B) a freshly prepared one. These two series have a different dependence of activity on the amount of iron sulphate added². In Figure 7 the Fe/Ru atom ratio obtained from ESCA analysis is plotted against the nominal Fe/Ru atom ratio in the initial solution used for precipitation. (All valence states are included in the ESCA data). Series A catalysts give values ≈ 0.03 higher than the theoretical data, but if subtracting this amount, which corresponds to the corrosion products, from all points one obtains a good agreement with the theoretical line. Evidently the ESCA data

correlate well with the actual composition. This implies that the series A catalysts are of a rather homogeneous character. Series B catalysts show a strong deviation from those in series A in that much lower Fe/Ru ratios are obtained. One difference between these two series is that in the stock solution (A) Fe^{3+} probably dominates, whereas in the freshly prepared solution (B) Fe^{2+} dominates. Upon precipitation these will form different iron hydroxides. If these have a considerably larger particle size in the B-series, the ESCA analysis should overestimate the ruthenium content. Generally, if mixing two powders with very different particle size, the ESCA analysis will overestimate the component with small particle size due to a packing and screening effect.

During precipitation mixed iron-ruthenium hydroxides are formed as well. Considering the solubility products²⁵ which are $\approx 10^{-14}$ for $\text{Fe}(\text{OH})_2$, $\approx 10^{-38}$ for $\text{Fe}(\text{OH})_3$, $\approx 10^{-38}$ for $\text{Ru}(\text{OH})_3$ and $\approx 10^{-44}$ for $\text{Ru}(\text{OH})_4$ it seems likely that series A initially contains a mixed hydroxide to a larger extent than series B.

In Figure 8 the rate of hydrogenation of benzene and the maximum yield of cyclohexene are shown as a function of the Fe/Ru atom ratio observed by ESCA. The reaction rate (Figure 8a) decreases linearly with increasing iron content. Both series A and B fall on the same line. However, when plotted against the nominal ratios two different curves are obtained². The maximum yield of cyclohexene (Figure 8b) shows a narrow maximum around an Fe/Ru ratio of 0.16 and both series A and B fall on the same curve in contrast to when they are plotted

against the nominal ratios. Thus it is clear that there is no difference in the catalytic performance of catalysts in series A and B when comparing samples with the same Fe/Ru ratios in the surface. An explanation to these results could be the different sizes of the iron hydrous oxide particles in series A and B suggested above. If series B yields larger particles the amount needed to poison a certain surface area is larger in this series. Consequently a larger nominal Fe/Ru ratio is needed in series B to obtain the same poisonous effect as in series A. If the iron hydrous oxide particles screen the underlying catalyst's surface from the ESCA analysis, the Fe/Ru ratios could be interpreted as the ratio of blocked to free surface. It is not known how large these particles are, only that they are X-ray amorphous, that is smaller than around 3 nm. It is very tempting to assume that the dispersion is high, because then the blocking effects could be discussed in terms of ensembles.

The maximum yield of cyclohexene is obtained at an Fe/Ru ratio of 0.16. That is every 6th Ru atom is blocked. Above this poisoning level the probability of forming ensembles of six Ru atoms, needed for planar adsorption of benzene, decreases rapidly. The decrease in selectivity above an Fe/Ru ratio of 1/6 can be interpreted as a decrease in the rate of formation of cyclohexene to the rate of formation of cyclohexane from cyclohexene. As will be shown below various other factors are of importance too, and the increase in selectivity at Fe/Ru ratios 0-0.16 are interpreted in other terms. The fact that the rate of hydrogenation of benzene decreases with the addi-

tion of iron supports the model of surface blocking by iron oxides.

Washing the Fe-Ru catalysts with concentrated HCl was performed in order to remove the hydrous oxides. As revealed in the Fe $2p_{3/2}$ peak (Figure 9) the iron hydrous oxides are dissolved and the metallic iron remains in the sample. Considering in addition that it apparently is stable towards oxidation we suggest that the iron is alloyed to the ruthenium metal. In Figure 10 it is shown that the iron metal content increases with the total iron content. With HCl washing the total iron content reduces drastically. The apparent increase in the metallic iron content probably depends on the fact that when dissolving the hydrous oxides, the underlying Fe-Ru bimetallic particles are uncovered and thereby give a greater contribution to the signals observed in the analysis. It is suggested that the bimetallic Fe-Ru particles are partly embedded in or covered by iron hydrous oxides. This is also in agreement with the observation that the percentage of metallic iron increases with decreasing iron content for the samples washed with water.

Pourbaix diagrams²⁰ suggest that metallic iron should not appear in our system, although the equilibrium stability area for metallic iron is close to the working conditions. Since iron in fact is detected, we suggest that in the mixed iron-ruthenium hydrous oxides - present initially - iron is made more easily reducible. Similar observations have been reported for PtFe²⁶ and PdFe²⁷ supported catalysts, in which the

reduction of the iron component is facilitated and bimetallic clusters are formed. The Fe-Ru bimetallic particles are therefore originating from the Fe-Ru mixed hydroxide, while the original iron hydrous oxide phase is still present after hydrogenation.

3.4 Influence of hydrogen and benzene coverage on selectivity

In an earlier paper² we discussed the increased selectivity for cyclohexene when the hydrogenation of benzene is performed on a poisoned ruthenium surface. The high selectivity was considered to be caused by poisonous species blocking certain active sites leaving others as doublets. We have now come to the conclusion that the catalyst surface consists of an Fe-Ru alloy and various iron oxide phases. All reactants, the organic molecules benzene and cyclohexene and hydrogen, are known to be chemisorbed on unpoisoned Ru-surfaces. The amount of hydrogen adsorbed on an Fe-Ru alloy is decreasing sharply with increasing iron content²³. This has also been observed in our experiments as will be shown below. Since the selective hydrogenation of benzene to cyclohexene is a reaction which is favoured by a low hydrogen coverage, the increased selectivity can partly be explained by the decreasing hydrogen coverage on the alloy phase. In an attempt to adsorb hydrogen on a 100% Fe catalyst, consisting of α -FeO(OH) and Fe_3O_4 according to X-ray analysis, we found that no hydrogen was adsorbed. Consequently the part of the surface of active catalysts which is covered by iron oxides is inactive in the hydrogenation reaction. Literature data indicates a lower amount

of chemisorption of benzene on iron than on the noble metals²⁸. Alloying of Ru with Fe thus probably results in a lower benzene coverage.

In summary, the decreased rate and the increased selectivity at low iron contents is caused by a decrease in active surface area due to a blocking by iron oxide phases and a decreased hydrogen and possibly benzene coverage on the Fe-Ru alloy phase.

3.5 Surface area and pore structure

Catalysts were coprecipitated from aqueous solutions of FeSO_4 and RuCl_3 as described above. The influence on the surface area of the amount of iron was investigated. Table 2 shows the surface area (S_{BET}) which decreases with the amount of iron added. Without iron addition the surface area is around $108 \text{ m}^2\text{g}^{-1}$ and it decreases to $56 \text{ m}^2\text{g}^{-1}$ with an iron addition of 40%. The t-method was also applied and the surface areas obtained by this method were in good agreement with S_{BET} . The t-method also showed that the catalysts did not contain any micropores and this explains the good agreement between S_t and S_{BET} . The surface area measured by adsorption of H_2 decreases in a linear fashion with the increasing amount of iron from $108 \text{ m}^2\text{g}^{-1}$ without iron to $39 \text{ m}^2\text{g}^{-1}$ at 40% iron. The reproducibility of the catalyst preparation is quite good as indicated in Table 2.

For the FeSO_4 preparation the pore volume, measured as the amount of nitrogen adsorbed at 77 K and $p/p_0=0.95$ and which includes pores with a radius of 23 nm or less, decreases con-

tinuously with increase in the percentage of iron. For this preparation V_{CUM} and V_{LIQN} - obtained in pore size distribution calculations⁷ - are also in good agreement with each other.

The concentration of ruthenium(III)chloride in the precipitation solution has an effect on the pore volume (compare catalysts without iron in Table 2). The pore volume for these two unpoisoned catalysts shows that a lower concentration gives a larger pore volume. The porosity is high and is 0.82 for the unpoisoned and 0.80 for the coprecipitated catalyst.

Figure 11 illustrates the surface area contributions for catalysts poisoned with ferrous sulphate in pores of different sizes. Except for pores with a radius of less than 2 nm the surface area contained in each pore size interval decreases with increasing percentage of iron.

The pore size distributions for the catalysts poisoned with ferrous sulphate are illustrated in Figure 12. The lower plot shows pores between 4 and 20 nm radius. The distribution is wide with several maxima. It is evident that the structure of the non-poisoned catalyst is retained but that the volume of pores of 4-20 nm pore radius decreases as the amount of iron increases. The upper plot concerns pores with a radius below 5 nm. The pattern is more complex and for pores with a radius below 3 nm the maxima are shifted and are also altered in their magnitude in a way not directly dependent on the amount of iron present.

Both the total surface area (S_{BET}) and the active surface area (S_{H_2}) decrease continuously with increasing iron content of the catalyst. When no iron is added the whole surface adsorbs hydrogen dissociatively. With increasing iron content the fraction of the total surface which is not adsorbing hydrogen increases and amounts to 8% at 5% Fe and to 30% at 30% Fe.

Figure 13 illustrates the specific rate of hydrogenation of benzene ($\text{rate}/S_{\text{H}_2}$) at a conversion of 10%. The rate decreases faster than S_{H_2} with increasing iron content especially above 20% Fe. This is to be expected since the larger ensembles necessary for the chemisorption of benzene are more easily poisoned than the hydrogen adsorption sites. Unfortunately we were not able to measure this quantity but the discussion on adsorption above points to a considerable poisoning effect of both iron and iron oxides on the adsorption of benzene.

3.6 Particle size

Figure 14 illustrates the particle size distributions for catalysts poisoned by different amounts of ferrous sulphate. The catalysts were all used in the hydrogenation of benzene in the aqueous phase at around 390 K and 3.3 MPa H_2 and yielded different amounts of the desired intermediate cyclohexene. The distributions are given as weight % contributed for particle diameters in different intervals. The distributions are wide and the non-poisoned catalyst consists of particles with diameters from less than 5 up to 50 μm . As the amount of iron increases the fraction of larger particles decreases considerably thereby decreasing the surface average diameter. At the

addition of 30% iron no particles larger than 25 μm were detected.

Figure 15 illustrates the surface average particle diameter for catalysts poisoned with ferrous sulphate and ferric chloride. The size is independent of the amount of iron up to 15% for ferrous sulphate and up to 20% for ferric chloride preparations. At higher iron additions the particle size decreases with the amount of iron and is slightly smaller when the catalyst is poisoned by ferrous sulphate than when poisoned with ferric chloride.

The above mentioned results were obtained from micrographs taken on catalysts stored in their mother liquor for 14 days. A number of measurements were also performed with catalysts which were photographed within 15 minutes after the samples were withdrawn from the reaction vessel. These results show that the actual particle size within the reactor is only about half that indicated in Figure 15. Since it is impossible to measure the particle size in the reactor during the hydrogenation these latter values will be assumed to be the correct ones. The particle size was also determined from SEM micrographs for a catalyst precipitated at room temperature and poisoned with 20% ferrous sulphate and was found to be 12 μm .

3.7 Pore diffusion effects

Pore diffusion limitations for consecutive reactions normally result in a decrease in the yield of the intermediate. It has

been demonstrated before^{1,2} that the hydrogenation of benzene to cyclohexene in an alkaline aqueous phase is somewhat limited by diffusion of hydrogen through the liquid film surrounding the gas bubble. It is thus highly probable that pore diffusion through the liquid film around the catalyst particle are important too.

In order to assure that isothermal conditions prevailed within the catalyst particle the temperature rise was calculated according to Carberry²⁹ for the unpoisoned catalyst, which exhibit the highest reaction rate. The effective thermal conductivity of the pellet was estimated as described³⁰ from data given in Table 3. The overall temperature gradient between the center of the catalyst particle and the surrounding bulk phase was then calculated to be only 0.06 K at the highest rate. The catalyst can thus be assumed to be isothermal which simplifies the calculation of effectiveness factors.

The pore size distributions reported above show that iron additions decrease the amount of pores of radii between 5 and 20 nm. This results in a lower mean pore diameter at increasing iron content. The diameter is 8 to 12 nm for the poisoned catalyst and this value is high enough not to cause any greater changes in the effective diffusivity of such small molecules as hydrogen and benzene. The effect of this change can thus be neglected.

The rate of hydrogenation is assumed to be first order in hydrogen concentration and benzene concentration in the aqueous phase. That is:

$$r_A = \eta \cdot k \cdot w \cdot C_A \cdot C_H$$

where r_A is the rate of hydrogenation of benzene, k the rate constant, w the catalyst loading, η the overall effectiveness factor and C_A and C_H the solubilities of benzene and hydrogen in the aqueous phase.

The overall effectiveness factor was calculated by a method described before³¹. Experimental rate data were measured at 390 K, 3.5 mPa H_2 , a catalyst loading of 0.11 g Ru, 1.19 M NaOH and a stirring rate of 1200 rev. min⁻¹ with the same apparatus and procedure as before². Catalyst particle diameters were measured in these hydrogenations as described above. The rate of hydrogenation at 10% conversion of benzene was used for the calculation of the effectiveness factor. The calculative method requires knowledge of mass transfer coefficients for benzene and hydrogen. The volumetric mass transfer coefficient for hydrogen, k_{La} , was determined experimentally². The mass transfer coefficient in the liquid particle interphase was calculated by a method given by Levins and Glastonbury³². The physico-chemical and other data given in Table 3 were calculated from published data.

The decrease of hydrogen concentration in the gas-liquid film was never greater than 2% of the solubility of hydrogen for iron additions of 0-10%. The resistance of the gas-liquid film decreases to negligible low values at higher iron additions. The film around the catalyst particles offers a greater resistance and the decrease in concentration of both hydrogen and benzene amounts to 20-27% at low iron additions decreasing rapidly to 0.3% at 30% iron.

Figure 16 illustrates the overall effectiveness factor as a function of the iron content of the catalyst. Since the particle diameter is constant up to 15% iron the effectiveness factor increases but very slowly with the iron content as a result of the decreasing rate of hydrogenation. At low iron contents the effectiveness factor is around 0.2. Above 15% iron it is increased rapidly as a result of both the decreasing particle size and the decreasing rate of hydrogenation. At iron additions above 25% the effectiveness factor exceeds 0.9 and at 30% the rate is controlled by the surface reaction itself ($\eta=0.98$).

Figure 17 illustrates the yield of cyclohexene as a function of the overall effectiveness factor. The maximum yield of cyclohexene increases rapidly from 5 to 10% at iron contents between 0 and 15%. Since in this region the effectiveness factor is almost constant the increase must be an effect of the increased poisoning of the catalyst surface as indicated in the poisoning model described above. At iron contents between 15 and 25% the effectiveness factor is markedly increased

and at the same time the maximum yield of cyclohexene is increased from 10 to 14%. This increase is thus a result of two factors, the increased poisoning and the decreased pore diffusion limitation. At iron additions above 25% the effectiveness factor is increased slightly from 0.87 to 0.98 but the yield is decreasing greatly from 14 to 4.5% caused by severe blocking of the sites for planar adsorption of benzene. The rate is decreasing very rapidly above 25% iron as well confirming that the active sites are blocked to a great extent.

4. Conclusions

The chemical composition of a Fe-Ru catalyst used in the hydrogenation of benzene to cyclohexene have been determined using X-ray diffraction and ESCA analysis. The X-ray diffraction yields lines for Ru-metal only for iron contents below 30%. Above this content lines from iron oxides appear as well. FeSO_4 and FeCl_3 preparations give magnetite, Fe_3O_4 , and goethite, $\alpha\text{-FeO(OH)}$, respectively. The formation of an Fe-Ru alloy is indicated by the interplanar spacings, which decrease linearly with iron additions up to 30%. The amount of the added iron which forms an alloy is estimated to be around 30% and the rest is most likely present as X-ray amorphous iron oxides below 30% iron. XRD data give information on crystalline compounds in the bulk whereas ESCA yields information on compounds in a surface layer of depth 1-3 nm. ESCA showed that at iron contents below 30% the catalyst surface consisted of a Fe-Ru alloy and an iron oxide phase. The quantitative data

showed a good correlation between surface and bulk compositions when the catalyst was made from a stock solution of FeSO_4 .

Adsorption of H_2 and N_2 revealed that both the BET surface area and the area capable of adsorbing H_2 decreased with increased iron content. The fraction of the surface that does not adsorb H_2 increases with the iron content and is 30% at 30% iron. Since the rate of hydrogenation decreases faster than S_{H_2} does, we conclude that benzene adsorption on the catalyst is decreasing rapidly too.

The addition of iron induces a change in the pore system. This change is not large enough to cause any significant altering of the effective diffusivities of benzene and hydrogen. However, on increasing iron content the catalyst particle size is greatly reduced. This causes an increasing effectiveness factor and an increased yield of cyclohexene. The net effect of pore diffusion is to limit the yield of cyclohexene at least for poisoning levels below 25% Fe.

The influence of iron on the maximum yield of cyclohexene was shown to be caused by two main processes. The yield is lowered when the hydrogenation is performed under pore diffusion limitation, and the yield is increased by poisoning of the catalyst surface by different poisonous iron species. The effect of the poisons can be explained if the hydrogenation of benzene is assumed to follow two different routes. The hydrogenation of benzene to cyclohexene requires four hydrogen atoms and the direct route to cyclohexane requires six hydrogen

atoms. It was shown above that the hydrogen coverage of the catalyst was decreased when the iron content was increased. This would obviously favour the route to cyclohexene thereby increasing the selectivity. This first effect is observed in the whole iron content range studied here.

The second effect, decreasing the yield of cyclohexene at iron contents above the optimal one, is the decreased adsorption of benzene. The planar π -adsorption of benzene is expected to require larger ensembles than the π -adsorption of cyclohexene. These larger ensembles are more easily destroyed on poisoning than the smaller ones with the effect that the benzene molecules are excluded from the surface while the cyclohexene ones are still able to react. This obviously leads to a decreased yield of cyclohexene as verified experimentally.

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Table 1. Binding energies and half widths^a (eV) of Fe 2p_{3/2} and O 1s core lines for some iron compounds and ruthenium-iron catalysts

<u>Sample</u>	<u>Fe 2p_{3/2}^b</u>	<u>O 1s</u>
Fe-foil, Ar ⁺ ion-etched	706.6 (2.8)	
Same sample, after passivation in air at 25°C.	710.4-706.6 ^c	531.2-529.3 ^e
Fe ₃ O ₄	710.8 (5.4)	530.2 (3.2)
Fe ₂ O ₃	710.6 (5.2)	529.4 (2.1)
FeO(OH)	711.0 (5.5)	530.8 (3.4)
Fe-Ru catalysts, Series A, Used in hydrogenation ^d .	710.2-706.4 ^c	532.2-529.5 ^e
Fe-Ru catalysts, Series B, Used in hydrogenation ^d .	709.8-706.3 ^c	532.0-529.7 ^e
Fe-Ru catalyst precursor, Series B	709.9 (6.0)	532.0-529.6 ^e

a FWHM within paranthesis

b Taken at peak maximum

c Shoulder

d Ruthenium in the metallic state according to Ru 3d_{5/2} B.E.²
No S 2p line was observed.

e Broad asymmetric structure with a clear indication of
several oxygen species.

Table 2. Adsorption of H_2 and N_2 on $FeSO_4$ coprecipitated^a Fe-Ru catalysts

Iron content Fe/ (Fe+Ru)	Surface area ($m^2 g_{cat}^{-1}$)				Pore volume ($cm^3 g_{cat}^{-1}$)		Porosity
	(Atom %)	S_{AREA}	S_{BET_1}	S_{H_2}	S_{BET_2}	S_t	Total
0	-	-	108.1	107.7	107.6	107.8	-
	-	-	111.7 ^b	-	-	102.7	-
10	-	-	101.4	107.7	105.7	98.8	0.366
	-	-	100.8	93.8	109.0	-	0.317
	97.3	-	-	-	-	-	-
20	-	-	91.8	-	-	-	-
	-	-	94.1	72.2	94.9	89.9	-
30	-	-	75.2	56.6	81.0	-	-
	-	-	59.8	-	-	58.6	-
40	51.9	56.4	38.8	59.0	-	-	-

^a Catalysts coprecipitated from a $0.71 g l^{-1}$ $RuCl_3$ hydrate solution at 353 K in 1.19 M NaOH.

Aged 1 h under H_2 flow of $50 cm^3 min^{-1}$. Reduced in the aqueous phase at 373 K and 3.5 MPa H_2 for 1 h inside the reactor. Total pore volume measured at $p/po = 0.98$. S_{CUM} , V_{CUM} and V_{LIQN} calculated for $p/po \leq 0.95$.

^b Catalyst precipitated from a $5 g l^{-1}$ $RuCl_3$ hydrate solution.

Table 3. Physical properties and constants used in the masstransport calculations.

Property		Reference
Temperature	390 K	
Hydrogen pressure	3.3 MPa	
Viscosity of 1.19 M NaOH	0.306 mPa's	33
Density of 1.19 M NaOH	0.996 g cm ⁻³	34
Density of benzene	0.775 g cm ⁻³	35
Bulk diffusivity of H ₂	3.22·10 ⁻⁴ cm ² s ⁻¹	36
Bulk diffusivity of benzene	4.71·10 ⁻⁵ cm ² s ⁻¹	36
Solubility of H ₂	1.80·10 ⁻⁵ mol cm ⁻³ aq	37
Solubility of benzene	3.71·10 ⁻⁵ mol cm ⁻³ aq	38
Heat of hydrogenation of benzene	209 kJ mol ⁻¹	39
Thermal conductivity of 1.19 M NaOH	0.69 Wm ⁻¹ K ⁻¹	40
Thermal conductivity of the solid	115 Wm ⁻¹ K ⁻¹	41
Specific heat of 1.19 M NaOH	4.04 kJ kg ⁻¹ K ⁻¹	42
Catalyst loading	1.665·10 ⁻⁴ g Ru cm ⁻³ aq	
Particle density	1.952 g cm ⁻³	
Particle porosity	0.82	
Tortuosity factor	3	
Volumetric masstransfer coefficient for H ₂ , k _L a	7.7 s ⁻¹	
Stirrer speed	20 rev s ⁻¹	
Stirrer diameter	5.8 cm	
Tank diameter	10.8 cm	
Power number (2x45° pitched six-blade turbines)	2.0	
Particle diameter	13.3-6.5 μm	
Rate of hydrogenation at 10% conversion of benzene	1.1-0.04 mmol s ⁻¹ dm ⁻³ _{aq}	
Outer surface area of particles	0.618-1.26 cm ² cm ⁻³ _{aq}	
Mass transfer coefficient in the liquid-particle interphase		
for benzene	0.197-0.289 cm s ⁻¹	
for H ₂	0.915-1.487 cm s ⁻¹	

Figure 1

X-ray diffraction spectra for some Fe-Ru catalysts precipitated at 353 K and reduced at 373 K (A and B) and 318 K (C and D). Samples C and D were sintered by air exposure.

A. 60 atom % Fe. FeSO_4 coprecipitation preparation.

B. 30 atom % Fe. FeSO_4 coprecipitation preparation.

C. 100 atom % Ru.

D. 43,3 atom % Fe. FeCl_3 coprecipitation preparation.

□ Fe_3O_4 (magnetite), ● RuO_2 , ○ $\alpha\text{-FeO(OH)}$ (goethite).

Figure 2

The Ru-metal crystallite size as a function of the iron content for FeSO_4 coprecipitated unused catalysts.

○ X-ray line broadening, □ H_2 chemisorption.

Figure 3

The interplanar spacing in the Ru matrix as a function of the iron content for FeSO_4 coprecipitated Fe-Ru catalysts.

Figure 4

Fe $2p_{3/2}$ electron spectra for some iron compounds.

A. Fe-foil. Ar^+ ion-etched.

B. Same sample, after passivation in air at 25°C .

C. Fe_3O_4

D. Fe_2O_3

E. FeO(OH)

F. Used catalyst, series A.

Figure 5

O 1s electron spectra for some iron compounds.

A. Fe-foil after passivation in air at 25°C.

B. Fe_3O_4

C. Fe_2O_3

D. $\text{FeO}(\text{OH})$

E. Used Fe-Ru catalyst. Fe-Ru atom ratio = 0.38.

F. Used Fe-Ru catalyst. Fe-Ru atom ratio = 0.04.

G. Difference spectrum E-F.

Figure 6

Atom ratio O/Ru versus atom ratio Fe/Ru both obtained by ESCA analysis of used Fe-Ru catalysts.

Figure 7

Atom ratio Fe/Ru obtained by ESCA versus atom ratio Fe/Ru as prepared for used Fe-Ru catalysts. Samples washed with distilled water.

□ Preparation from a stock FeSO_4 solution. Series A.

○ Preparation from a freshly prepared FeSO_4 solution.

Series B.

● Samples washed with concentrated hydrochloric acid.

Figure 8

The rate of hydrogenation of benzene (a) and the maximum yield of cyclohexene (b) as a function of the atom ratio Fe/Ru as obtained by ESCA. Rate and yield data from ref.

(2). 1.123 mol benzene and 400 cm³ 1.19 M NaOH, 0.43 g Ru, 388 K, 3.5 MPa H_2 , 1200 rev. min⁻¹.

Figure 9

Fe $2p_{3/2}$ electron spectra for some Fe-Ru catalysts.

- A. Catalyst precursor.
- B. Used catalyst, washed with destilled water.
- C. Difference spectrum B-A.
- D. Used catalyst, washed once with concentrated hydrochloric acid.
- E. Used catalyst, washed twice with concentrated hydrochloric acid.

Figure 10

The atom ratio of iron metal to ruthenium (Fe^O/Ru) versus the total iron content to ruthenium (Fe^{tot}/Ru), for some Fe-Ru catalysts both obtained by ESCA analysis.

- Washed with destilled water.
- Washed once with conc. HCl.
- Washed twice with conc. HCl.

Figure 11

The cummulative surface area in different pore size intervals as a function of the amount of iron. $FeSO_4$ coprecipitated preparation. A 0%, B 10%, C 20%, D 30%.

Figure 12

The pore size distributions for catalysts with various iron content (atom %). $FeSO_4$ coprecipitated preparation. A 0%, B 10%, C 20%, D 30%.

Figure 13

Specific rate of hydrogenation of benzene as a function of iron content 1.123 mol benzene and 400 cm³ 1.19 M NaOH, 0.11 g Ru, 390 K, 3.3 MPa H₂, 1200 rev. min⁻¹.

Figure 14

The particle size distribution for catalysts with various iron content (atom %). FeSO₄ coprecipitated preparation. A 0%, B 10%, C 20%, D 30%.

Figure 15

The surface average particle diameter as a function of iron content for Fe-Ru catalyst. o FeSO₄, □ FeCl₃ coprecipitated used catalysts, stored in their mother liquor for 2 weeks. X FeSO₄ coprecipitated used catalysts, measured within 15 minutes ● Same treatment but measured by SEM.

Figure 16

Overall effectiveness factor as a function of iron content. 1.123 mol benzene and 400 cm³ 1.19 M NaOH, 0.11 gRu, 390 K, 3.3 MPa H₂, 1200 rev. min⁻¹.

Figure 17

Maximum yield of cyclohexene as a function of the overall effectiveness factor. 1.123 mol benzene and 400 cm³ 1.19 M NaOH, 0.11 g Ru, 390 K, 3.3 MPa H₂, 1200 rev. min⁻¹.

Figure 1

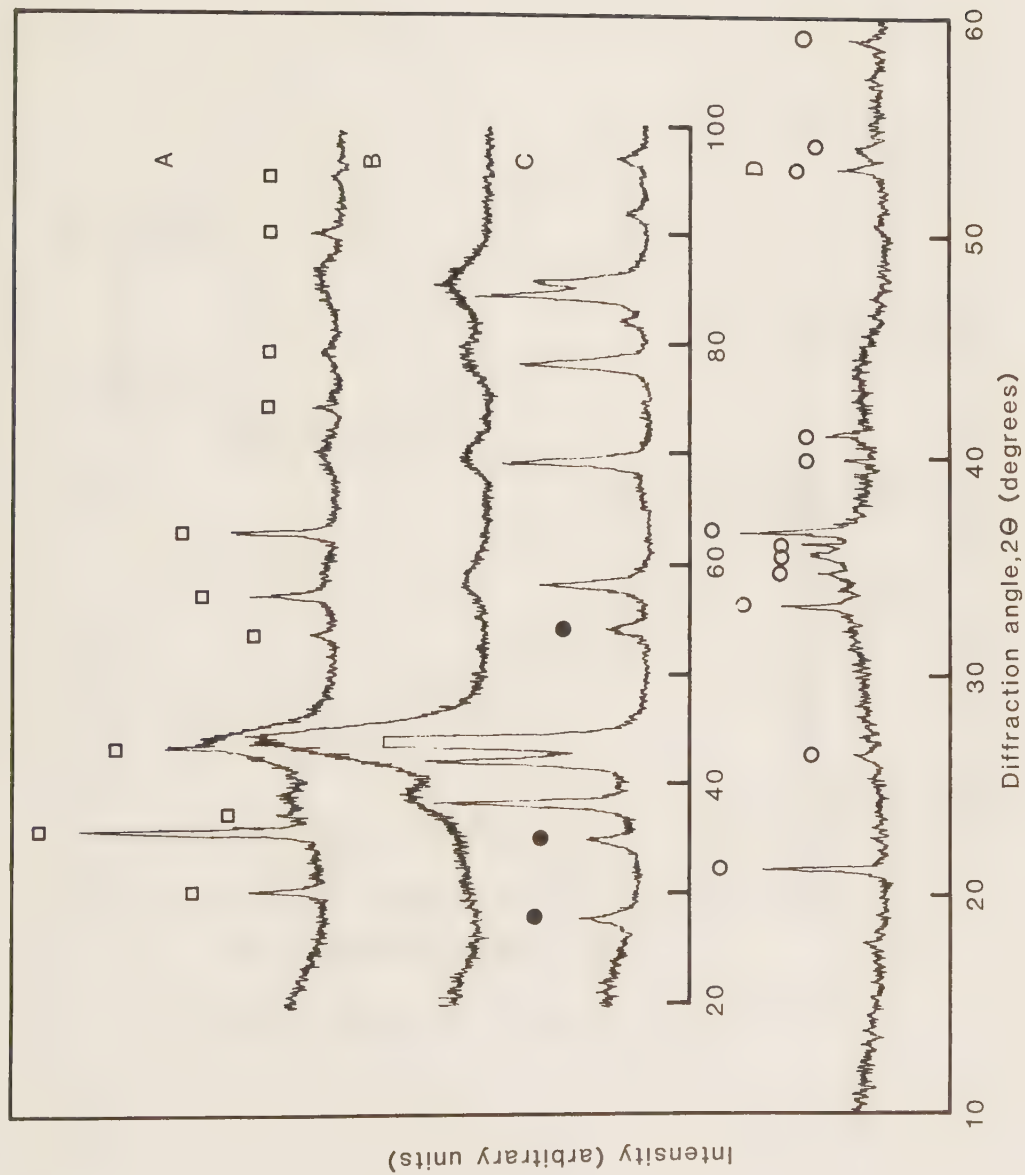


Figure 2

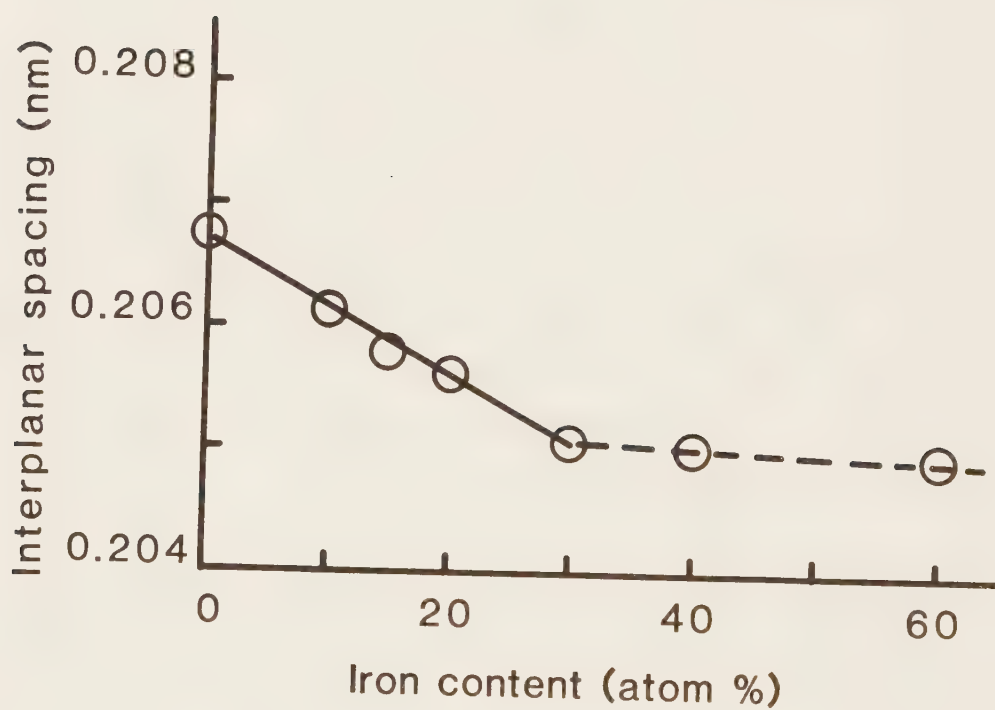


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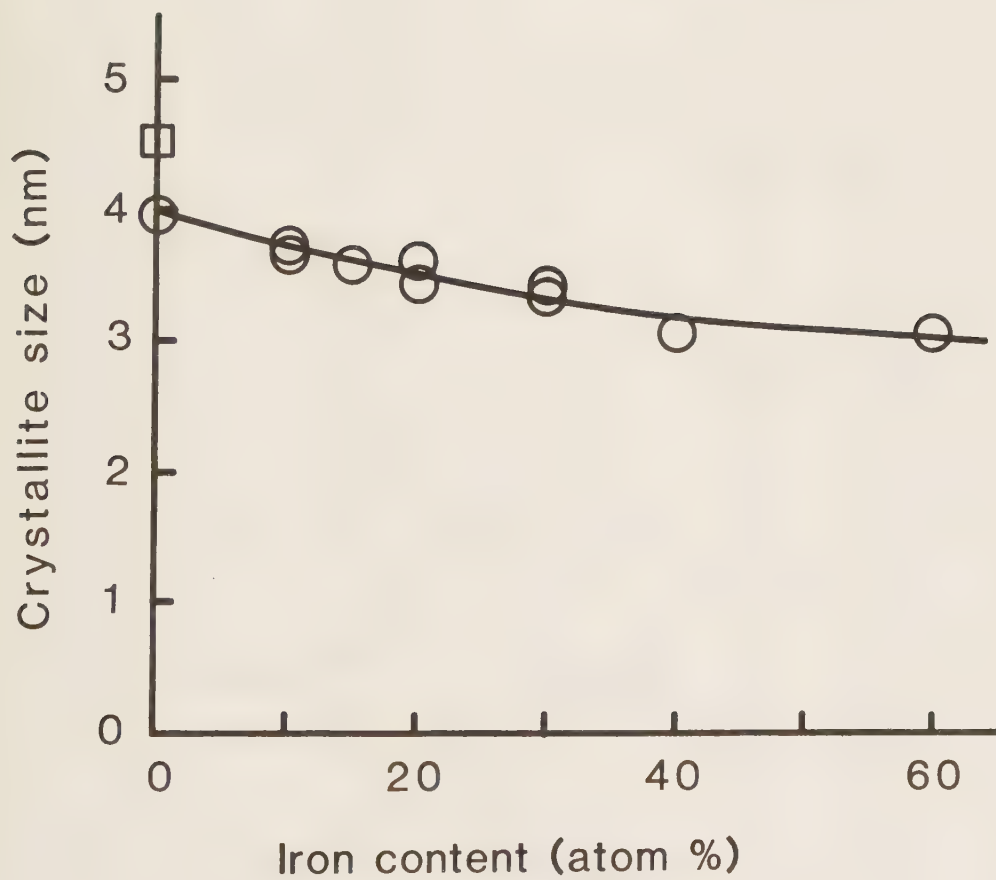


Figure 4

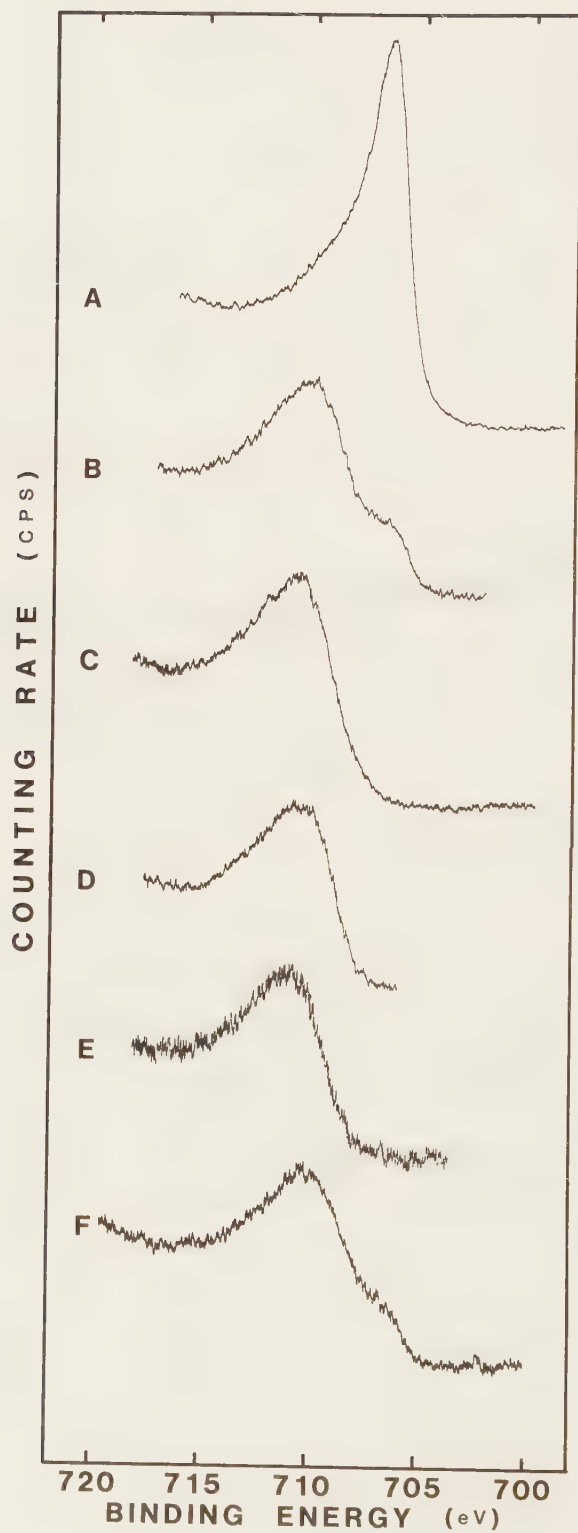


Figure 5

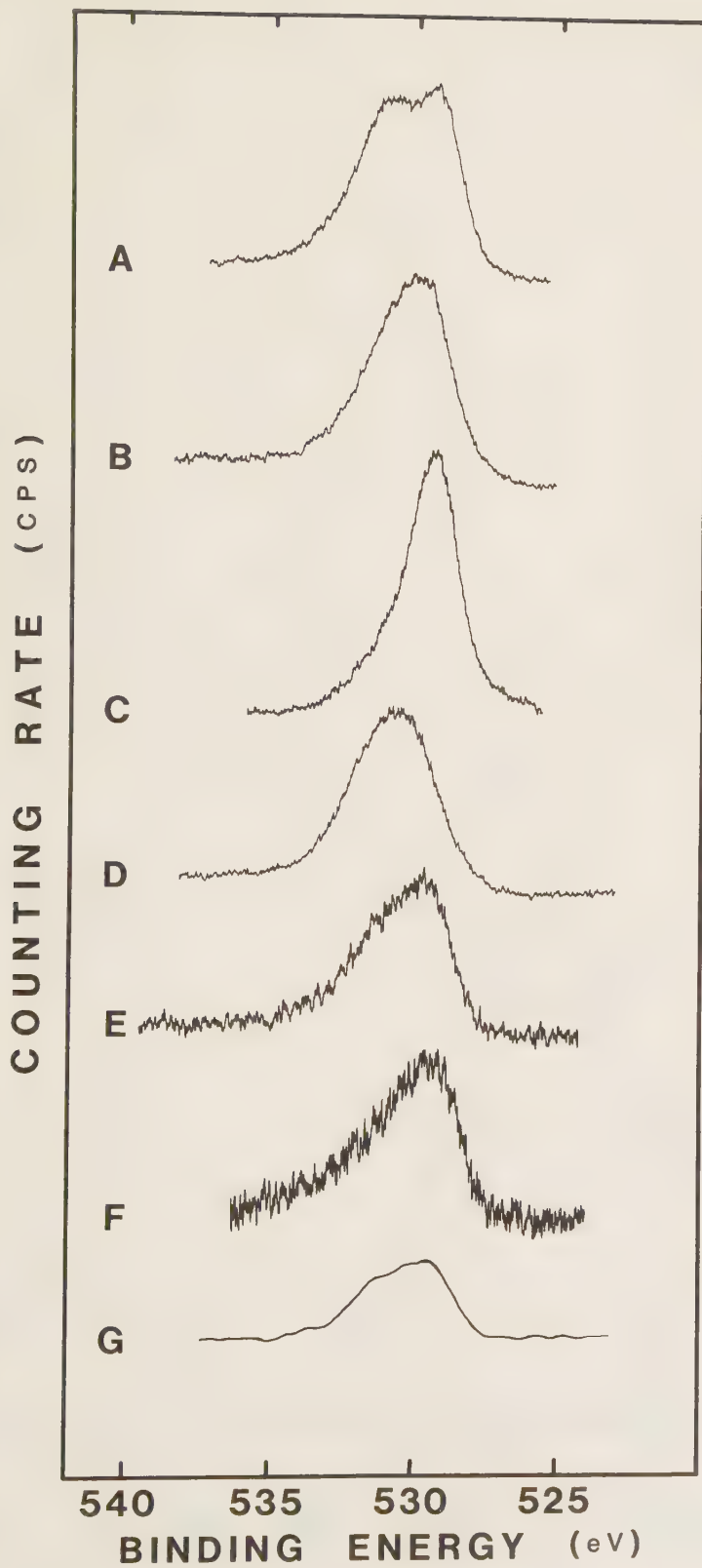
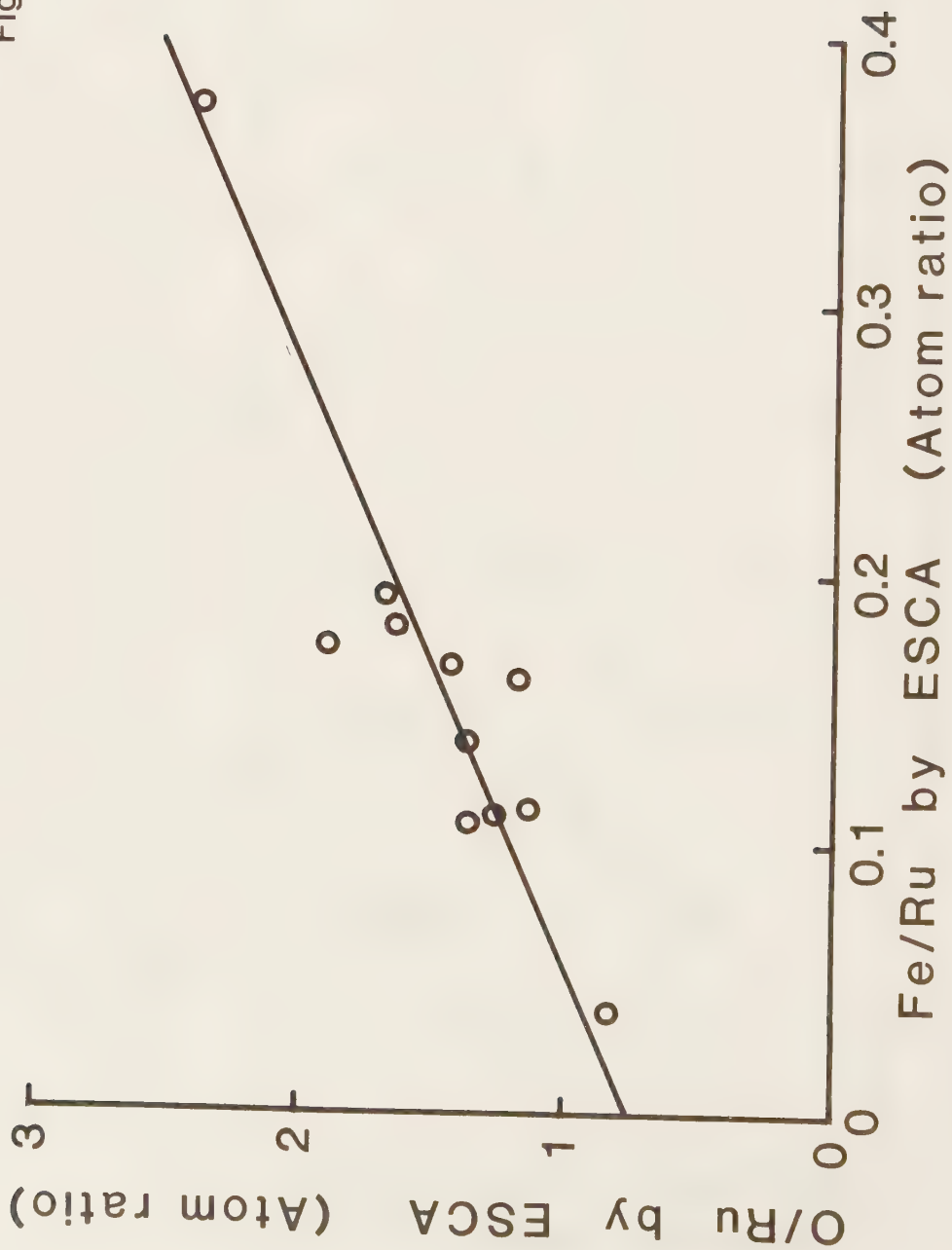


Figure 6



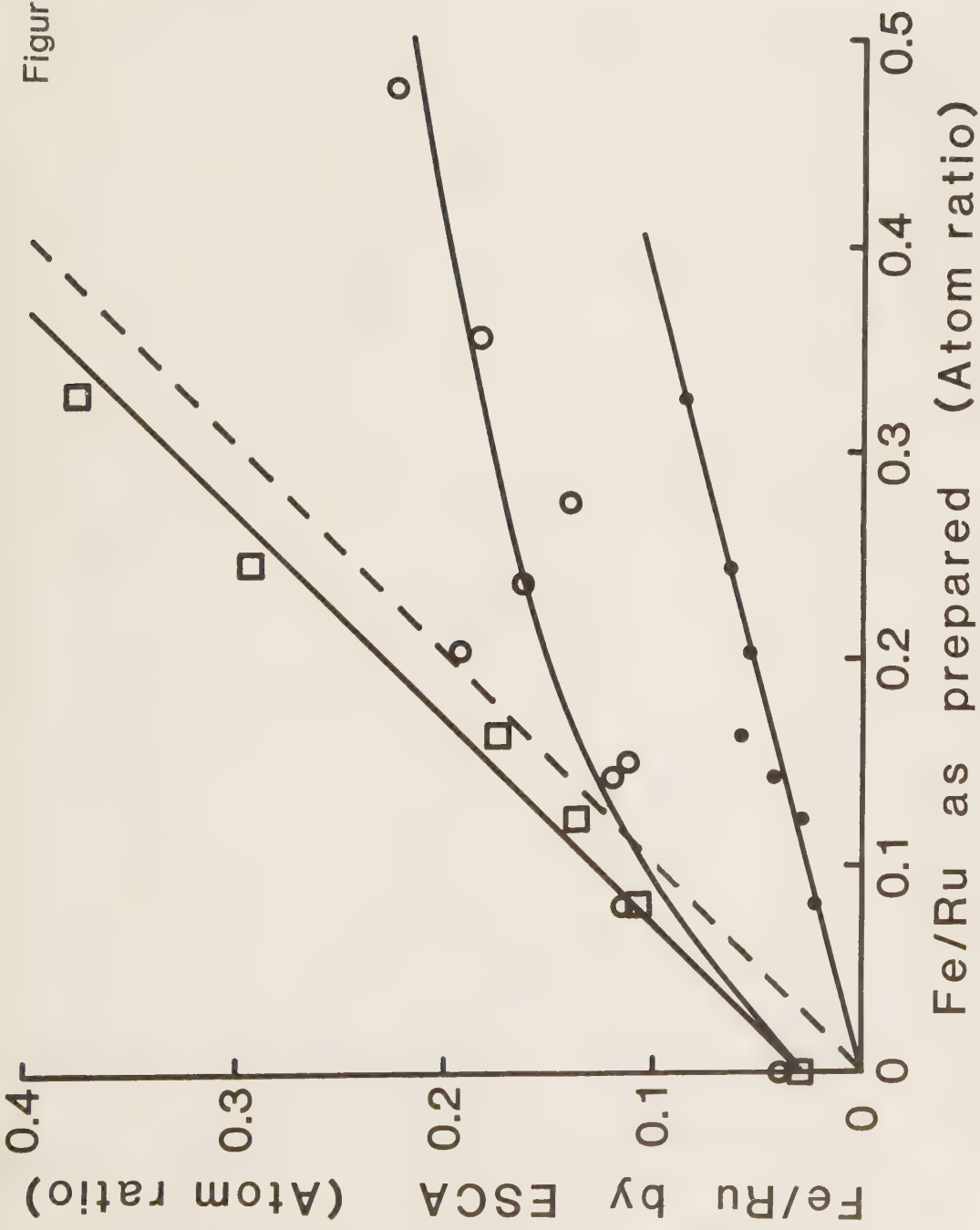


Figure 7

Figure 8

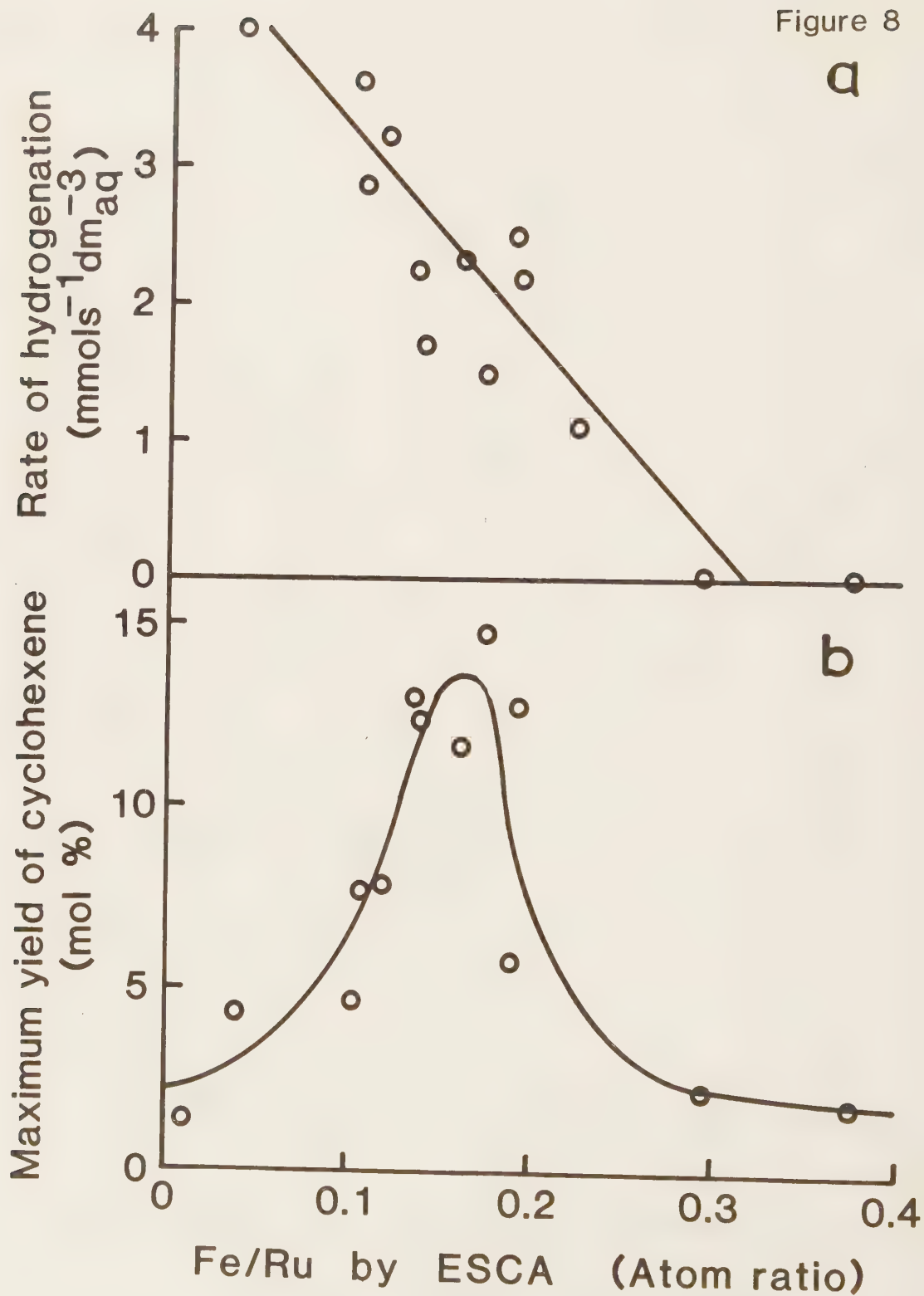


Figure 9

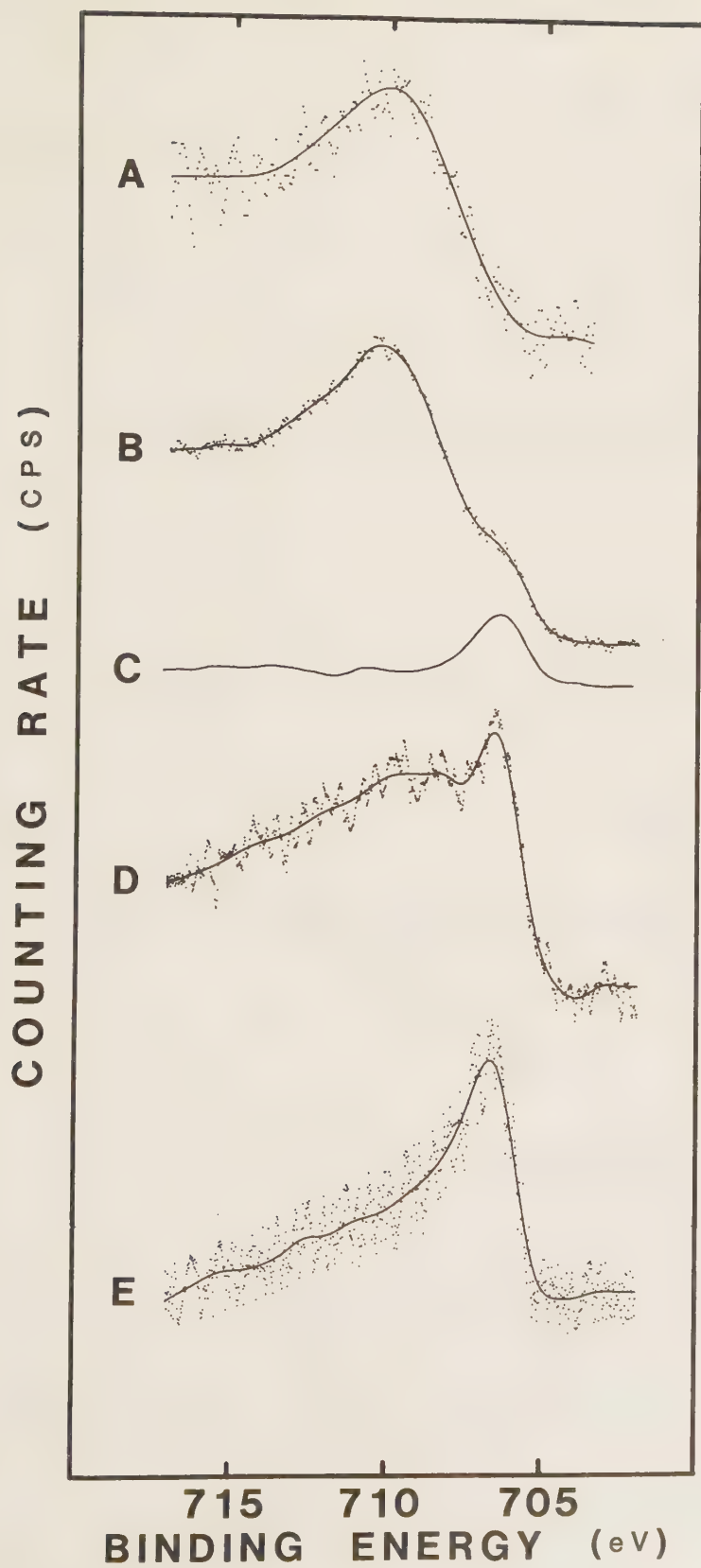


Figure 10

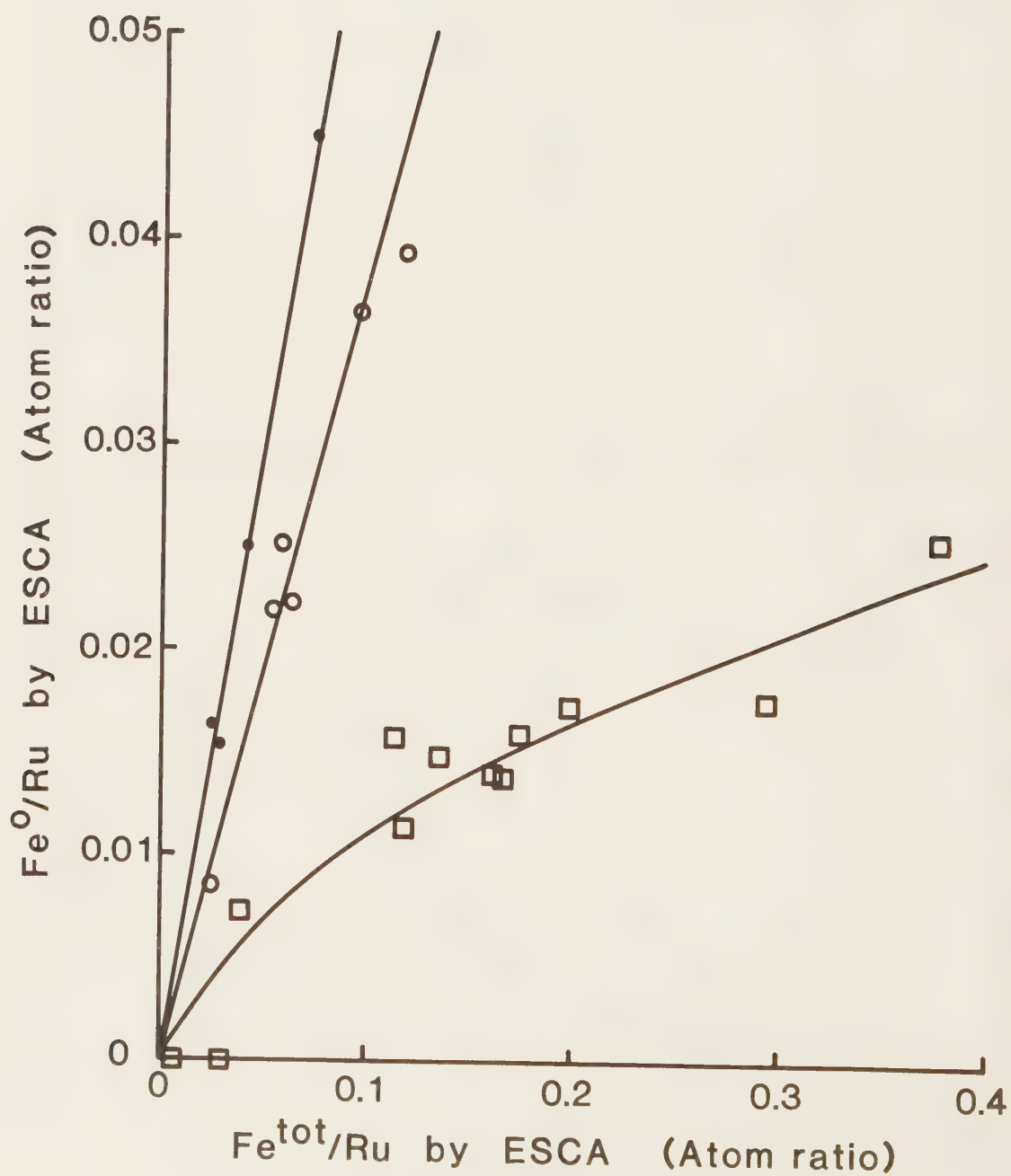


Figure 11

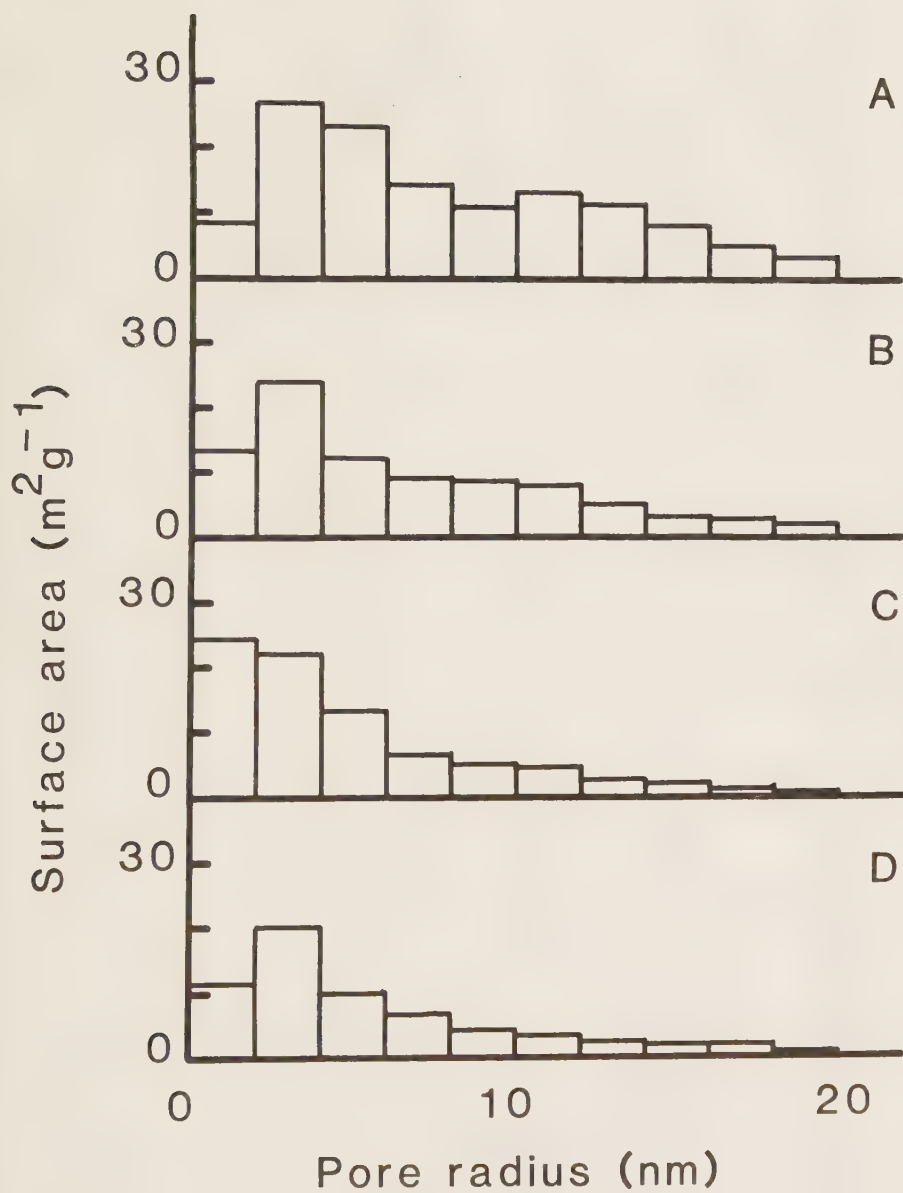
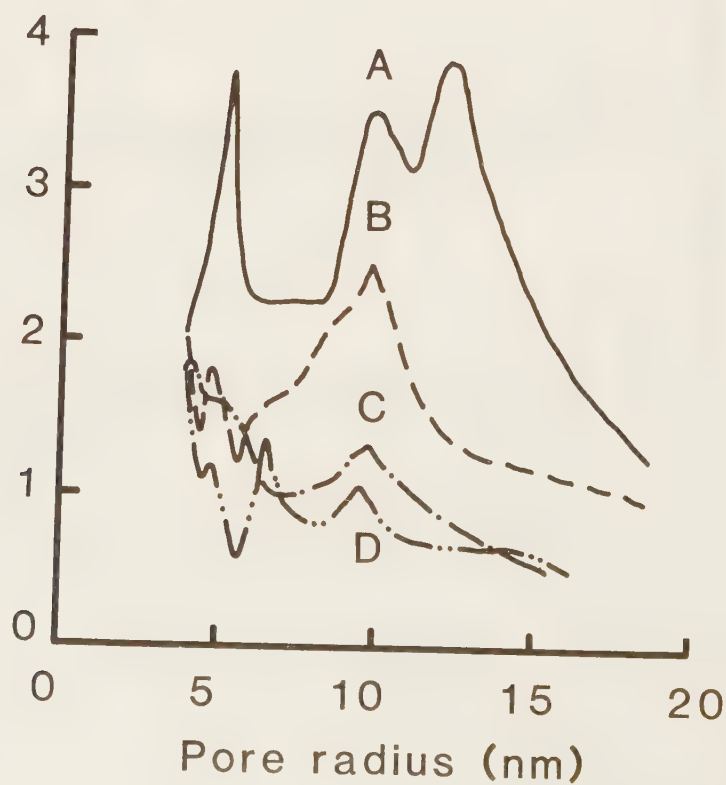
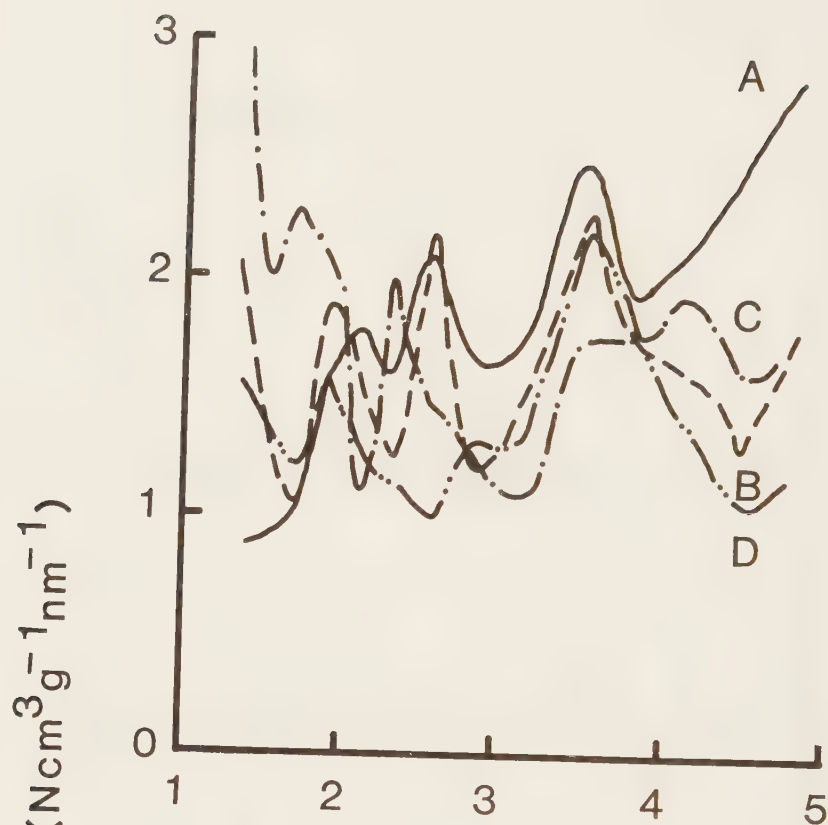


Figure 1



Specific rate of hydrogenation of benzene

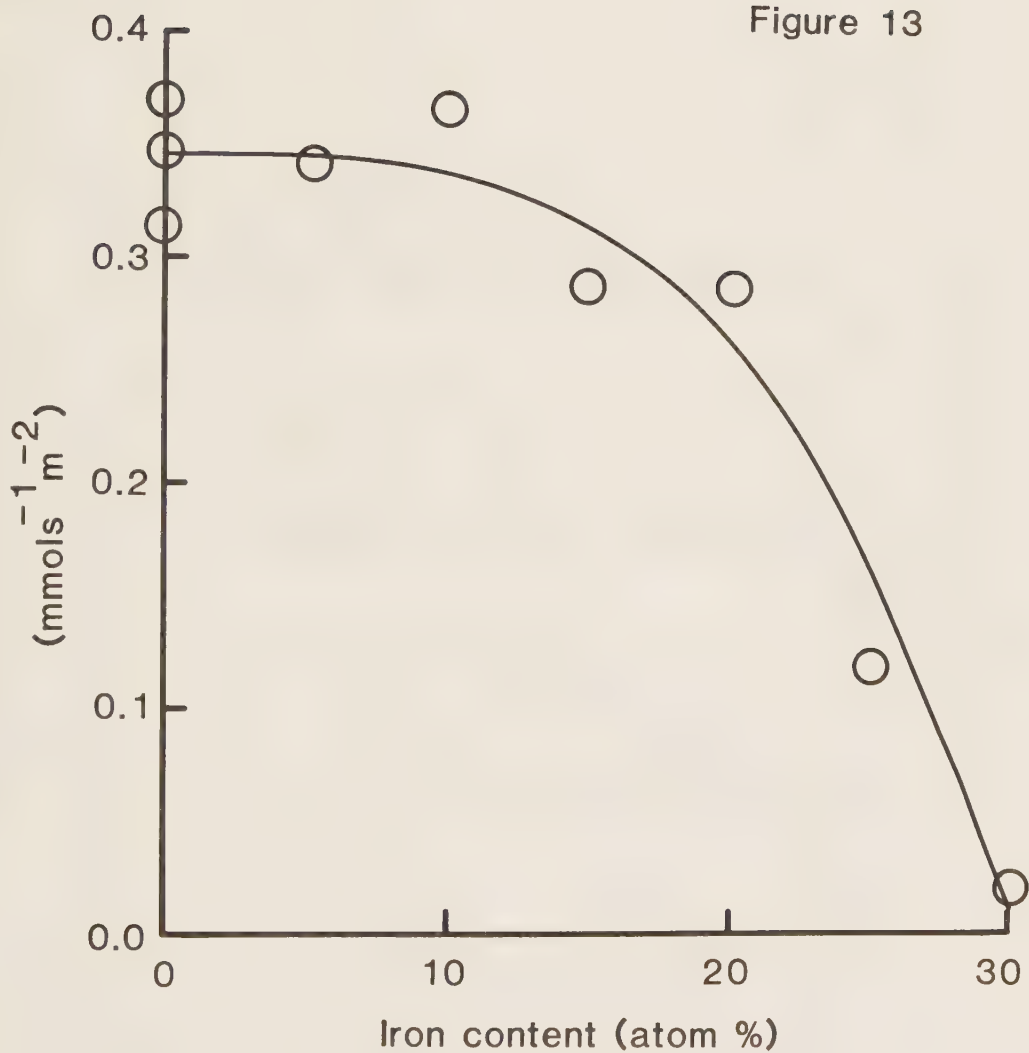


Figure 14

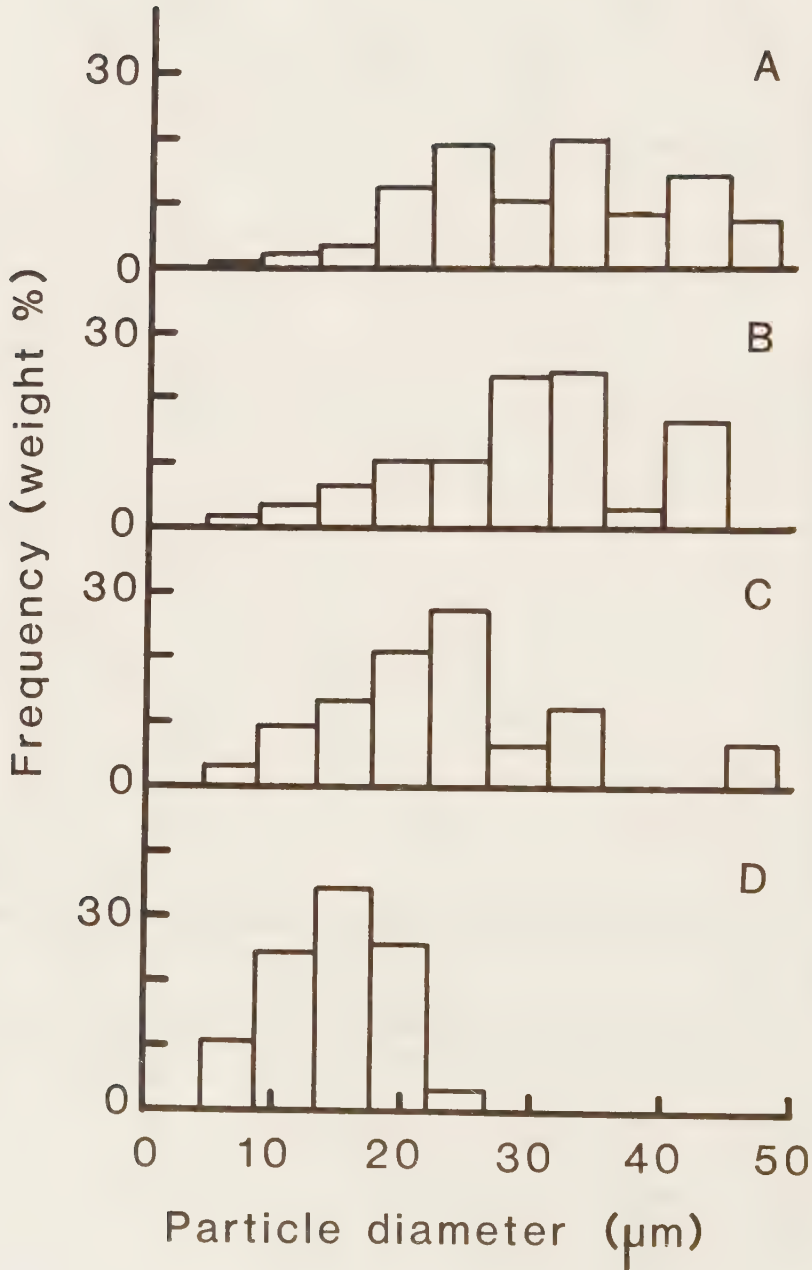


Figure 15

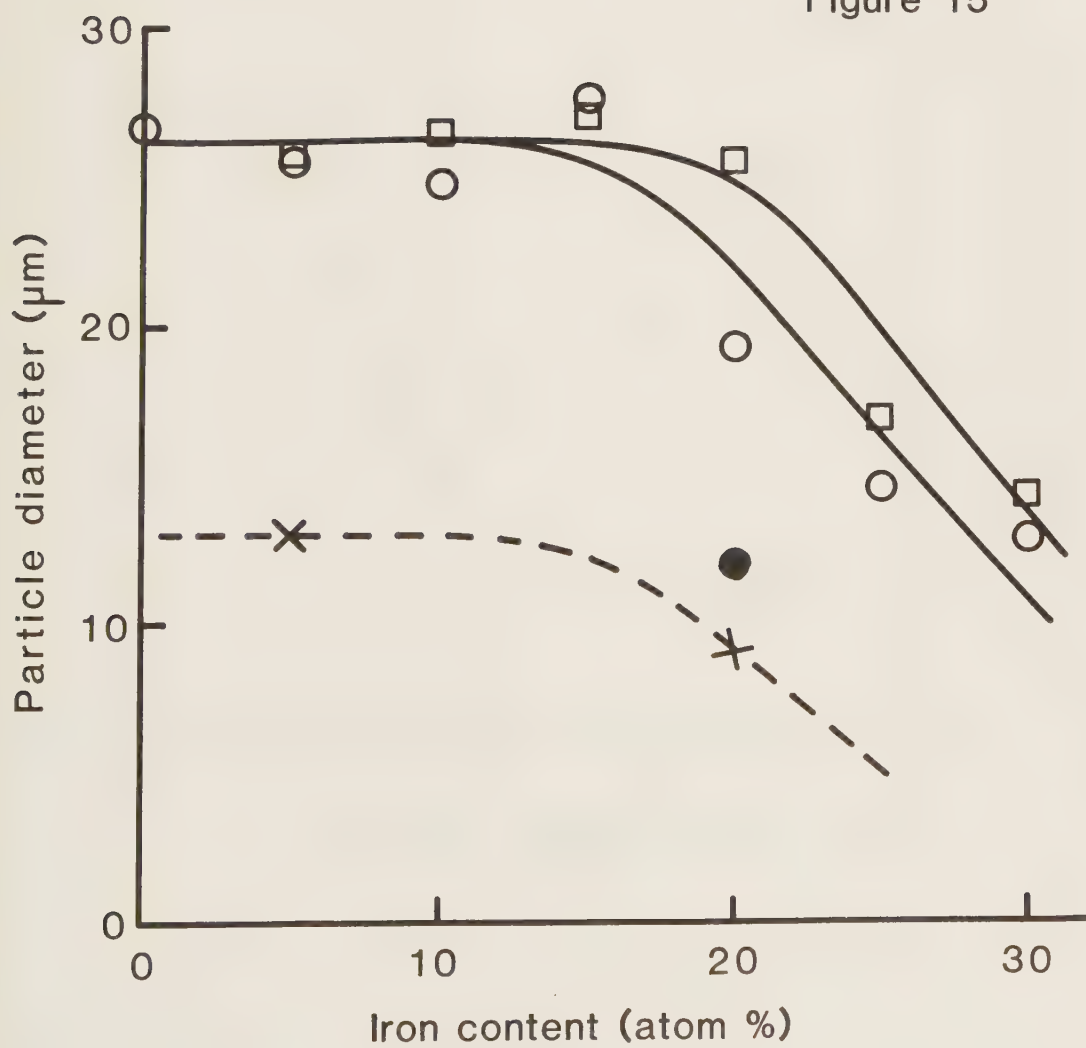


Figure 16

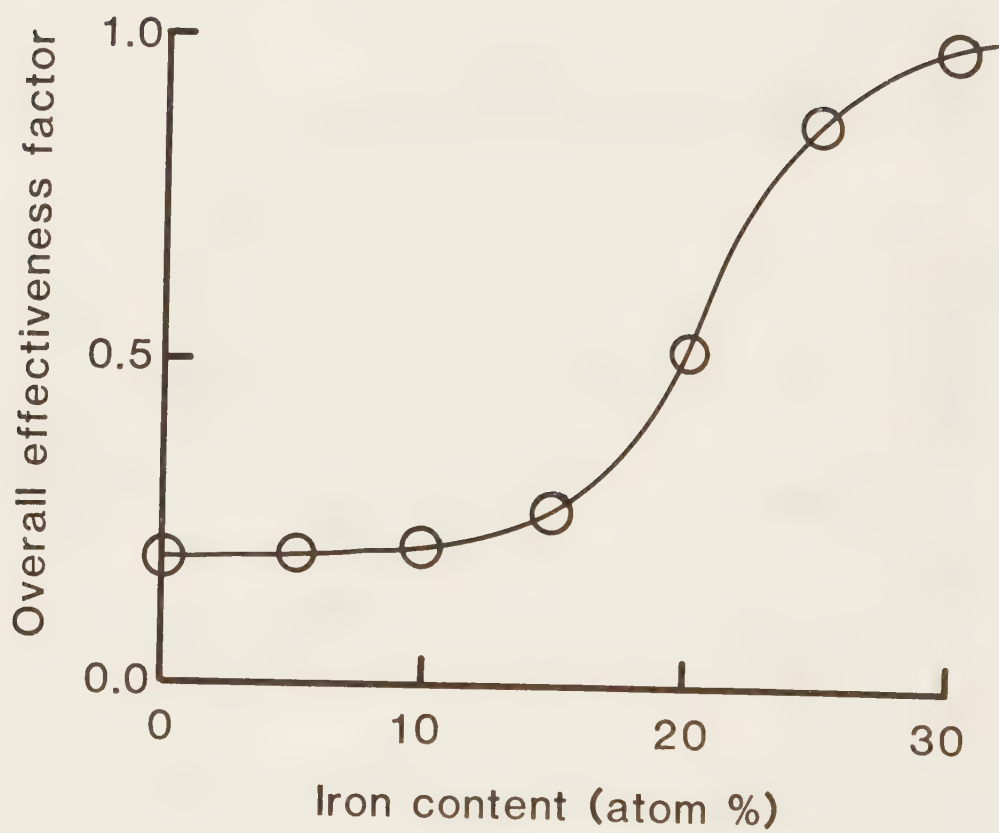
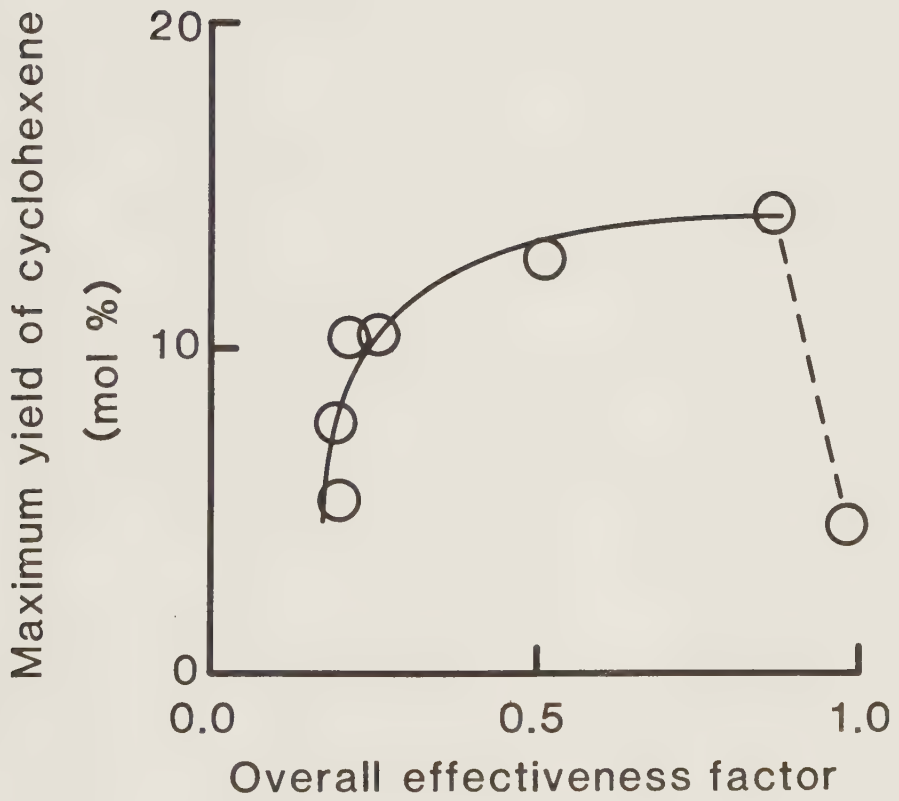


Figure 17



V

HYDROGENATION OF BENZENE TO CYCLOHEXENE ON AN
UNSUPPORTED RUTHENIUM CATALYST: An ESCA Study of
titanium poisoned catalysts.

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SYNOPSIS

ESCA data show that the addition of titanium to a ruthenium catalyst gives a catalyst containing some metallic ruthenium and a mixed titanium-ruthenium hydrous oxide. The ratio of ruthenium in the metallic form to ruthenium in the hydrous oxide form decreases with increasing titanium concentration. The poisoning effect of the titanium addition on the hydrogenation activity results from the reduced amount of ruthenium metal available.

1. Introduction

An increased interest in ruthenium as a catalyst for the selective hydrogenation of benzene to cyclohexene has recently been shown¹⁻⁶. To further our understanding of how the catalyst works we recently made an investigation on the texture and chemistry of pure Ru-catalysts⁷. It has been shown that poisoning of the catalyst by addition of iron and titanium compounds influences both the yield of cyclohexene and the reaction rate¹. The effects of the iron additions on the texture and chemistry of the catalyst were recently characterized by physical and chemical techniques⁸ and we have now extended these studies to an investigation of the titanium poisoned catalysts by X-ray photoelectron spectroscopy.

2. Experimental

2.1 Preparation

The materials used were ruthenium(III)chloride hydrate (Fluka AG, purum, 10-15% water), titanium(III)chloride solution (BDH Technical, 15% w/v TiCl_3), sodium hydroxide (EKA, 98.6%), and TiO_2 (Riedel-De-Haen AG, purum).

The catalysts were prepared by adding appropriate amounts of titanium(III)chloride to a stock solution of ruthenium(III) chloride in distilled water from which solids were precipitated in a Parr pressure reactor² following instantaneous addition of 9.6 M sodium hydroxide to a final

concentration of 1.19 M. After the hydrogenation experiments, the catalyst slurry was washed with several portions of 0.01 M NaOH, decanted and dried by evacuation at room temperature before ESCA analysis.

2.2 ESCA studies

The procedure for the ESCA measurements have been described elsewhere⁷. They were performed on an AEI ES200B electron spectrometer, equipped with an Al-anode (1486.6 eV). The full width at half maximum (FWHM) of the Au 4f_{7/2} line was 1.8 eV. Sample charging was corrected for with the Au 4f_{7/2} line at 83.8 eV. In the quantitative ESCA analysis - as described elsewhere² - the sensitivity factors were C 1s = 1, O 1s = 2.7, Ru 3d_{5/2} = 7.4 and Ti 2p_{3/2} = 4.8. Some spectra were digitized and smoothed⁹ on a Tektronix 4051 with a 4662 interactive digital plotter. A quadratic smoothing over a number of points taken as 0.7x(FWHM) was used¹⁰. End points which normally are lost were estimated with a linear least squares fit¹⁰. Some peak envelopes were simulated by adjusting the position and width of the selected Gaussian components until a correct fit in the least squares approximation of the magnitudes was obtained. The base line for the O 1s peak was approximated to a straight line. The Ru 3d peak showed a much higher slope in the base line and it was necessary to make allowance for this effect - arising from inelastic scattering - in the calculations¹¹.

3. Results and discussion

Catalysts prepared by precipitation of RuCl_3 and TiCl_3 aqueous solutions show great changes in activities and selectivities with the Ti/Ru ratio². Some catalysts used in the hydrogenation have been examined by ESCA to gain information on the chemical state of Ru and Ti. The atom ratio Ti/Ru as revealed by ESCA is shown in Figure 1 as a function of the bulk atom ratio Ti/Ru. With the sensitivity factors used there is a deviation of less than 10% from the theoretical Ti/Ru line. The fact that the Ti/Ru atom ratio by ESCA does not deviate much from the Ti/Ru atom ratio as prepared - and has a linear correlation - shows that Ti and Ru are present either in one phase with no surface segregation effects¹², or in two separate phases with comparable particle sizes¹³.

The binding energies for Ru $3d_{5/2}$, Ti $2p_{3/2}$ and O $1s$ are given in Table 1. The Ti $2p_{3/2}$ core line has a fairly constant value around 457.6 - 457.8 eV for the four catalysts with various Ti/Ru ratios, indicating the similarity of the Ti - compounds in these different catalysts. The O $1s$ line, however, changes very much as seen in Figure 2. Spectrum C, obtained with the catalyst with the highest titanium loading, clearly shows that there is one major oxygen component at 529.6 eV, which is the value obtained for lattice oxygen in TiO_2 . The component at 531.1 eV is assigned to hydroxide oxygen and the one at 532.7 eV to physisorbed water. The spectra A and B

in Figure 2, for the catalysts with Ti/Ru ratios of 0.23 and 0.58, show a much broader structure indicating a larger amount of the higher B.E. oxygen species. The structure is complicated by the fact that the samples with higher ruthenium content probably contain significant amounts of other oxygen-containing species in combination with ruthenium. However, it is clear that the amounts of the low and perhaps middle B.E. components are increasing with increasing titanium content. This would suggest the presence of TiO_2 or rather hydrated TiO_2 . It is known from Pourbaix diagrams¹⁴ that $\text{TiO}_2 \cdot \text{H}_2\text{O}$ and TiO_2 are the stable species under the hydrogenation conditions used. Further, hydrated TiO_2 upon ageing forms TiO_2 and water, even in aqueous media¹⁵. However, the Ti $2p_{3/2}$ B.E. are slightly lower than for TiO_2 (see Table 1). Considering that titanates have a Ti $2p_{3/2}$ B.E. lower by 0.4-0.7 eV than that found with TiO_2 ¹⁶, we suggest that a ruthenium titanate has formed in our samples. It is probably an ill-defined precipitate and should perhaps rather be called a mixed ruthenium - titanium hydrous oxide.

Considering the Ru $3d_{5/2}$ core line B.E., it is seen in Table 1 that apparently a continuous shift occurs from 279.9 up to 281.6 eV with the addition of titanium. The Ru $3d$ spectra are shown in Figure 3. It is evident that the Ru $3d_{5/2}$ line with an increased Ti/Ru ratio is broadened and shifted towards higher B.E. The spectra

are disturbed by the presence of the C 1s core line from carbon contaminations. The estimated C/Ru atom ratio increases with titanium addition from 0.2 up to 0.9 for the sample with the highest Ti/Ru ratio. However, this change is caused by the decreasing Ru-content since the C/(Ti+Ru) atom ratio remains fairly constant at around 0.2. The apparent continuous shift in the Ru $3d_{5/2}$ B.E. can be explained by the presence of two different ruthenium species with a change in their relative amounts for the four catalysts. The spectra in Figure 3 have been resolved into four Gaussian components representing Ru $3d_{3/2}$ and $3d_{5/2}$ for ruthenium hydroxide and for ruthenium metal and in addition two Gaussian components representing the C 1s line for carbon contamination. All components are added to the base line as described above. The C 1s lines are placed where usually observed, that is around 285 eV with a shoulder towards higher B.E. The interesting feature seen in the resolved spectra is that the ratio of ruthenium metal to ruthenium hydroxide is changing with titanium content. (See also Ru^O/Ru^{total} in Table 1). The ruthenium metal 3d line should be asymmetric due to the excitation of hole-electron pairs¹⁷, which is not expected for the ruthenium hydroxide. An estimation of this effect is given in table 1 where Ru^O/Ru^{total} ratios corrected for the asymmetric line shape are included. This was done by assuming that the same ratio of the two low B.E. Gaussian curves in the pure Ru-catalyst is re-

presentative of the asymmetric metal line shape for all samples. The result is only to give slightly higher ratios but the overall trend remains.

The addition of titanium prevents the reduction of all of the ruthenium and this indicates the presence of some mixed hydrous oxides. The preparation of the catalyst is performed with aqueous RuCl_3 and TiCl_3 which probably contain ions of the valence states +3 and +4. Since the solubility products^{15,18} are $\approx 10^{-38}$ for $\text{Ru}(\text{OH})_3$, $\approx 10^{-44}$ for $\text{Ru}(\text{OH})_4$ and $\approx 10^{-54}$ for $\text{Ti}(\text{OH})_4$ it seems likely that the initial precipitate partly consists of a mixed $\text{Ru}(\text{III,IV}) - \text{Ti}(\text{III,IV})$ hydrous oxide in addition to the individual hydroxides. Titanium(III)-hydroxide is easily converted to $\text{TiO}_2 \cdot \text{H}_2\text{O}$ by the oxygen present in the solution¹⁵. Since the titanium dioxide is not reduced under the present hydrogenation conditions it seems likely that the coprecipitated ruthenium hydroxide is not reduced either. However, any ruthenium hydroxide present as a separate phase would be reduced. From Table 1 one may deduce a Ti/Ru ratio for the mixed hydrous oxide which is close to one for the two catalysts with lower titanium additions. The mixed hydroxide could perhaps be regarded as a ruthenium titanate hydrate by analogy with co-precipitated Mg and Ti-hydroxides¹⁹. However, for those samples containing a surplus of titanium the Ti/Ru ratios for the mixed hydroxide is approximately 1.7 and 4 respectively, and it is then necessary that

the excess of titanium is present in a separate hydroxide phase.

In Figure 4 the dependence of the rate of hydrogenation on the amount of ruthenium metal taken as $\text{Ru}^{\text{O}}/\text{Ru}^{\text{total}}$ is shown. Since all batches contain the same amount of ruthenium and since the ESCA analysis reveals the surface content this ratio should be proportional to the amount of ruthenium metal available for catalytic hydrogenation. There is apparently a linear dependence of the hydrogenation rate on the amount of ruthenium metal. The fact that the line does not go through the origin can be explained by poisoning effects, caused by metallic species corroded from the reactor walls during the hydrogenation experiment.

In order to clarify this question the rate of dissolution of iron was measured at 366 K and recalculated to the hydrogenation temperature (389 K) as before¹. The rate of hydrogenation was then corrected for the poisonous effect of iron and these values are also shown in Figure 4 (dashed line). It is clear that this correction gives a much better correlation indicating that the rate of hydrogenation is proportional to the unpoisoned metallic Ru surface area.

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Table 1. Binding energies and half widths^a (eV) of Ru 3d_{5/2}, Ti 2p_{3/2} and 0 1s core lines and atom ratios of Ti/Ru and Ru^O/Ru^{total} for some titanium-ruthenium catalysts.

<u>Sample</u>	<u>Ru 3d_{5/2}</u>	<u>Ti 2p_{3/2}</u>	<u>0 1s^b</u>	<u>Ti/Ru</u>	<u>Ru^O/Ru^{total}</u>
Ru-catalyst precursor	281.5 (2.5)		531.1-529.4		
Ru-catalyst	279.9 (1.9)				0.84 (1) ^d
Ti/Ru catalyst (0.23) ^c	280.1 (2.5)	457.8 (2.8)	531.2 (5.7)	0.20	0.61 (0.73) ^d
Ti/Ru catalyst (0.58) ^c	280.4 (2.8)	457.7 (2.5)	531.0 (4.9)	0.44	0.52 (0.62) ^d
Ti/Ru catalyst (1.15) ^c	281.3 (3.4)	457.7 (2.1)	530.9 (4.7)	1.25	0.21 (0.25) ^d
Ti/Ru catalyst (2.81) ^c	281.6 (3.4)	457.6 (2.2)	530.2 (3.4)	3.17	0.18 (0.21) ^d
TiO ₂		458.5 (1.7)	529.6 (2.0)		

a FWHM within parenthesis

b Taken at half height

c Ti/Ru atom ratio as prepared

d Corrected for asymmetric line shape of the metal Ru 3d lines.

Figure 1

Atom ratio Ti/Ru obtained by ESCA analysis versus the atom ratio Ti/Ru as prepared.

Figure 2

O 1s electron spectra from some Ti-Ru catalysts with various Ti/Ru atom ratios (as prepared). A. 0.23, B. 0.58, C. 2.81 and D. TiO_2 . Spectrum C is resolved in three Gaussian components.

Figure 3

Ru 3d binding energy region electron spectra from some Ti-Ru catalysts with various Ti/Ru atom ratios.

A. 0, B. 0.23, C. 0.58, D. 1.15, E. 2.81

The spectra are resolved in two sets of two Gaussian curves (Ru $3d_{3/2}$ and Ru $3d_{5/2}$) representing ruthenium metal and ruthenium hydroxide respectively (Dashed lines). C 1s lines from carbon contaminations are presented by two Gaussian curves (Solid lines).

Figure 4

Rate of hydrogenation (from ref 2) versus atom ratio $\text{Ru}^{\text{O}}/\text{Ru}^{\text{total}}$ by ESCA for titanium poisoned catalysts.

○ measured by ESCA, ◻ corrected for the influence of corrosion products.

Figure 1

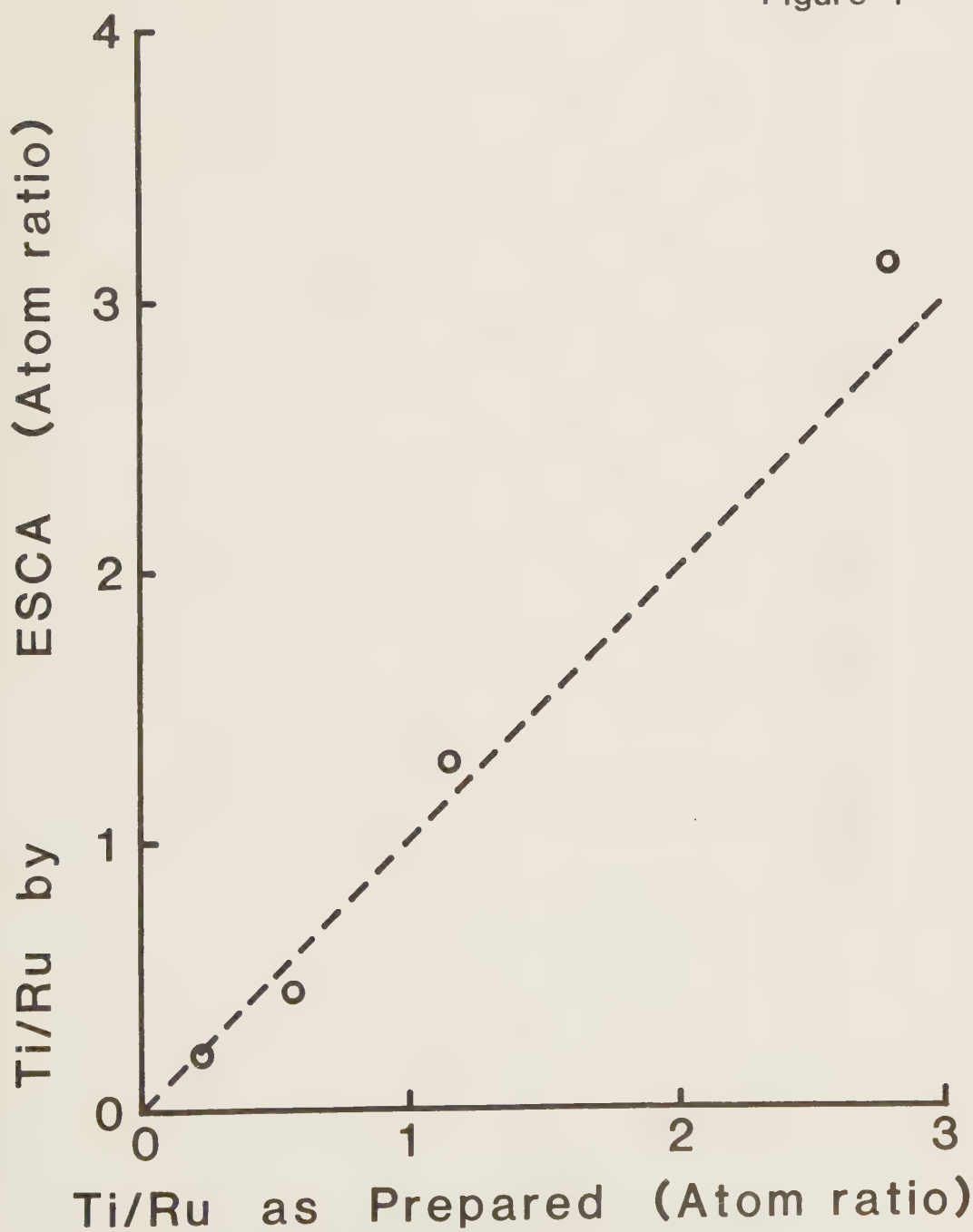


Figure 2

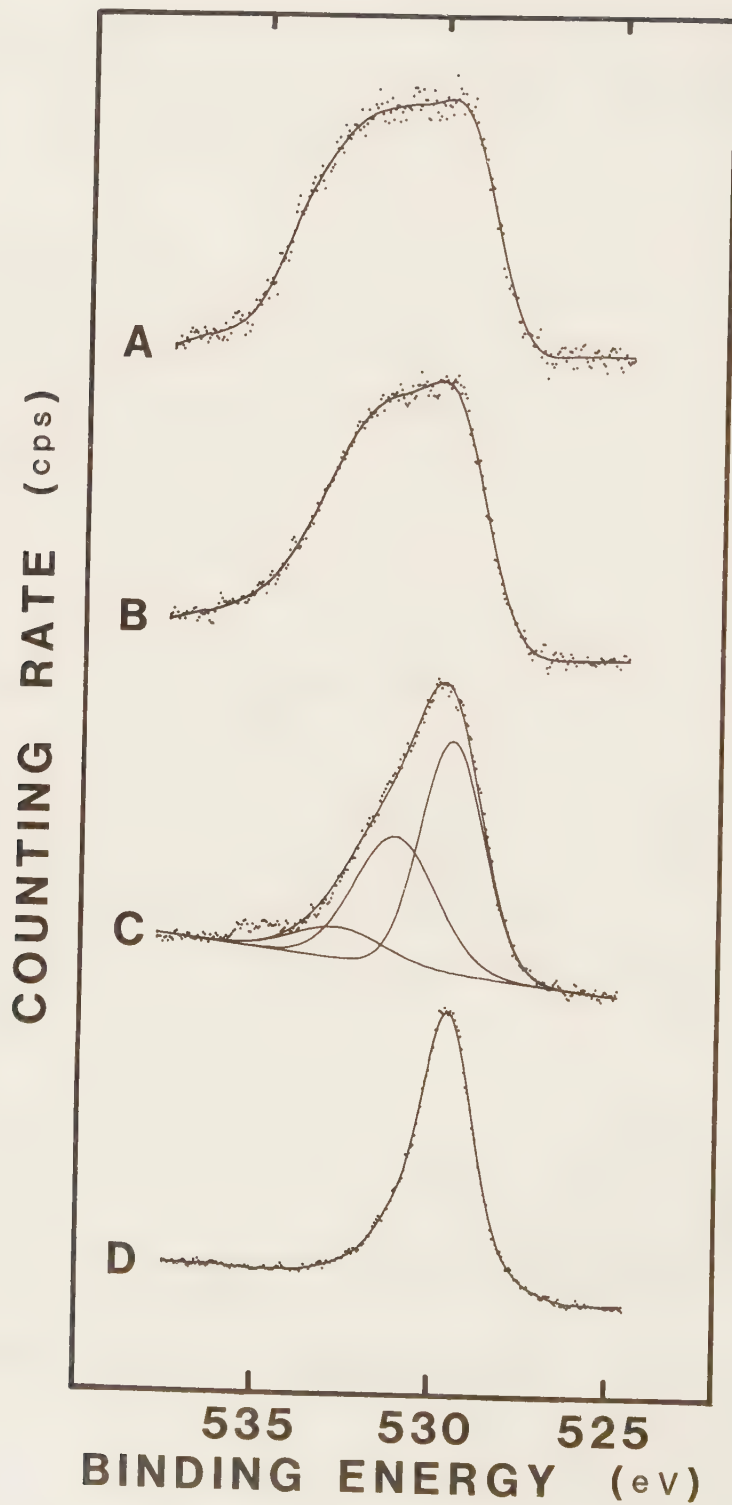
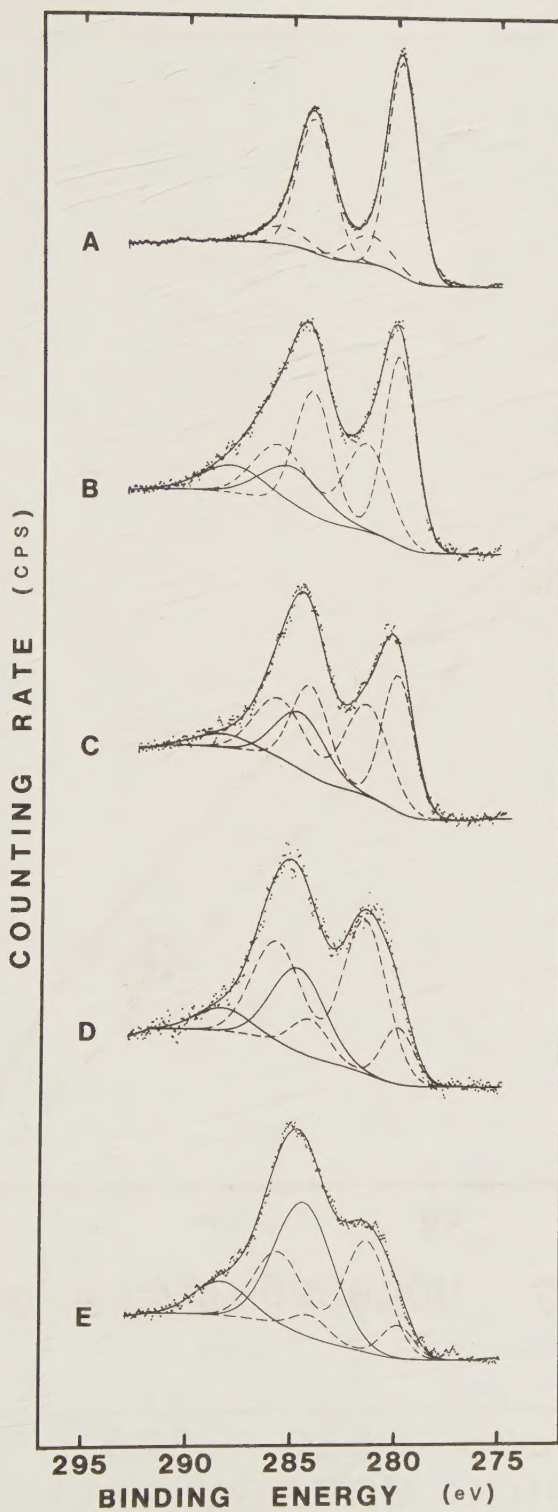


Figure 3



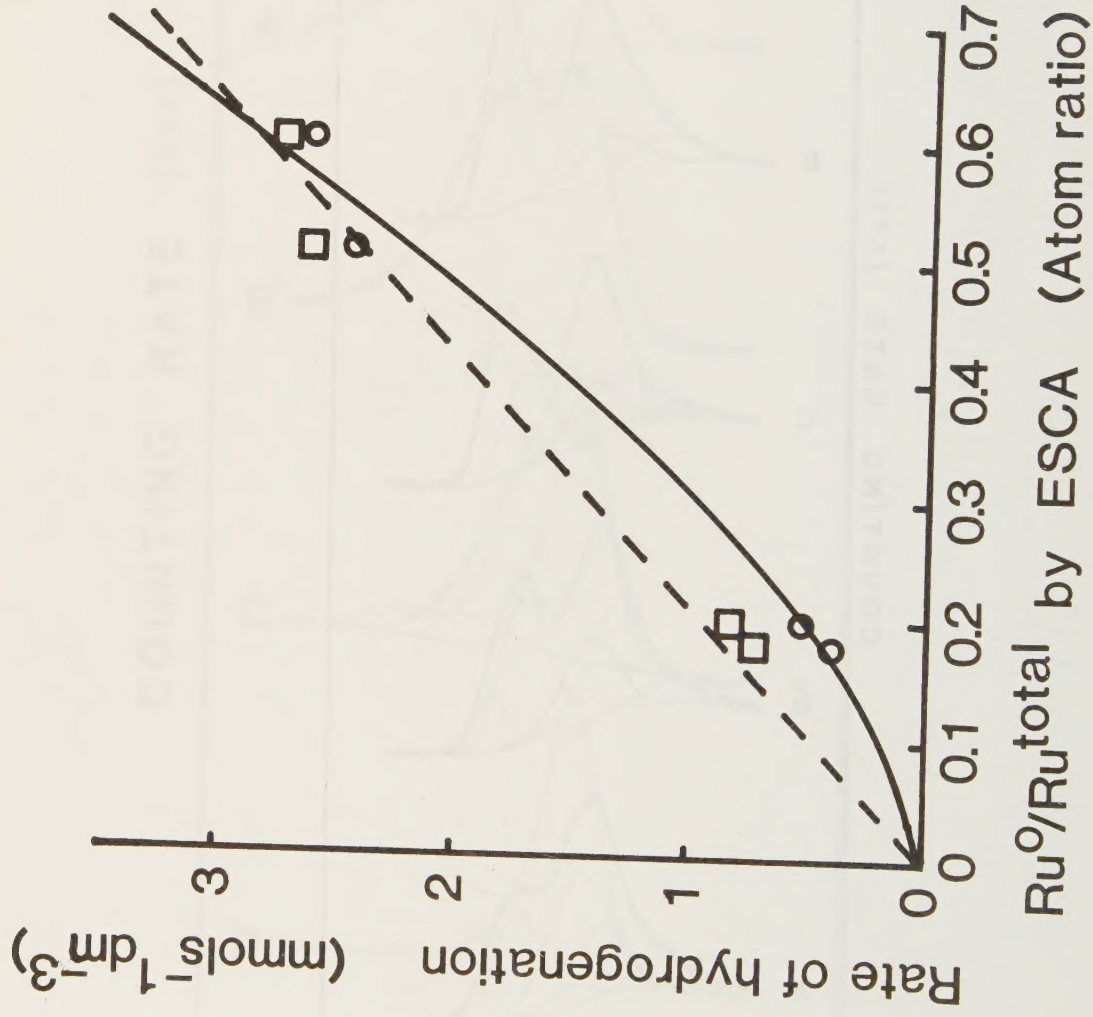


Figure 4

